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(54) Title: COMPOUNDS AND PHARMACEUTICAL COMPOSITIONS AS CATHEPSIN S INHIBITORS

(57) Abstract: The present invention relates to novel selective cathepsin S inhibitors, the pharmaceutically acceptable salts and *N*-oxides thereof, their uses as therapeutic agents and the methods of their making.

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# COMPOUNDS AND PHARMACEUTICAL COMPOSITIONS AS CATHEPSIN S INHIBITORS

## THE INVENTION

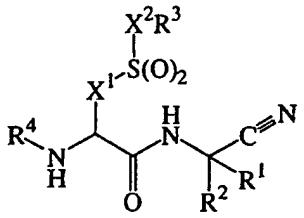
This Application relates to compounds and compositions for treating diseases associated with cysteine protease activity, particularly diseases associated with activity of cathepsin S.

## DESCRIPTION OF THE FIELD

Cysteine proteases represent a class of peptidases characterized by the presence of a cysteine residue in the catalytic site of the enzyme. Cysteine proteases are associated with the normal degradation and processing of proteins. The aberrant activity of cysteine proteases, e.g., as a result of increase expression or enhanced activation, however, may have pathological consequences. In this regard, certain cysteine proteases are associated with a number of disease states, including arthritis, muscular dystrophy, inflammation, tumor invasion, glomerulonephritis, malaria, periodontal disease, metachromatic leukodystrophy and others. An increase in cathepsin S activity contributes to the pathology and/or symptomatology of a number of diseases. Accordingly, molecules that inhibit the activity of cathepsin S protease are useful as therapeutic agents in the treatment of such diseases.

## SUMMARY OF THE INVENTION

This Application relates to compounds of Formula I:



I

in which:

$X^1$ and $X^2$ are both methylene or $X^1$ is ethylene and $X^2$ is a bond;

$R^1$ is hydrogen and $R^2$ is cyano, hetero($C_5$)aryl or ($C_{1-4}$)alkyl-substituted hetero($C_5$)aryl or both $R^1$ and $R^2$ are hydrogen, halo, ($C_{1-4}$)alkyl or $-X^3OR^9$, wherein $X^3$ and $R^9$ are as defined below, or $R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-8}$)cycloalkylene or ($C_{3-8}$)heterocycloalkylene;

$R^3$ is $-CR^5=CHR^6$ or $-CR^7=NR^8$, wherein $R^5$ and $R^6$ together with the atoms to which $R^5$ and $R^6$ are attached form ($C_{2-6}$)alkenyl, ($C_{5-12}$)cycloalkenyl, hetero($C_{5-12}$)cycloalkenyl, ($C_{6-12}$)aryl, hetero($C_{6-12}$)aryl, ($C_{9-12}$)bicycloaryl or hetero($C_{8-12}$)bicycloaryl and $R^7$ and $R^8$ together with the atoms to which $R^7$ and $R^8$ are attached form hetero($C_{5-12}$)cycloalkenyl, hetero($C_{6-12}$)aryl or hetero($C_{8-12}$)bicycloaryl, wherein $R^3$ optionally is substituted by 1 to 5 radicals independently selected from a group consisting of ($C_{1-4}$)alkyl, cyano, halo, halo-substituted ($C_{1-4}$)alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or ($C_{1-2}$)alkylene, $R^9$ at each occurrence independently is hydrogen, ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{10}$ is ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and

$R^4$ is $-C(O)X^4R^{11}$ or $-S(O)_2X^4R^{11}$, wherein $X^4$ is a bond, -O- or $-NR^{12}-$, wherein $R^{12}$ is hydrogen or ($C_{1-6}$)alkyl, and $R^{11}$ is (i) ($C_{1-6}$)alkyl optionally substituted by $-OR^{13}$, $-SR^{13}$, $-S(O)R^{13}$, $-S(O)_2R^{13}$, $-C(O)R^{13}$, $-C(O)OR^{13}$, $-C(O)NR^{13}R^{14}$, $-NR^{13}R^{14}$, $-NR^{14}C(O)R^{13}$, $-NR^{14}C(O)OR^{13}$, $-NR^{14}C(O)NR^{13}R^{14}$ or $-NR^{14}C(NR^{14})NR^{13}R^{14}$, wherein $R^{13}$ is ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl,

hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl, ($C_{9-12}$)bicycloaryl($C_{0-3}$)alkyl or hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl and $R^{14}$ at each occurrence independently is hydrogen or ($C_{1-6}$)alkyl, or (ii) ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl, ($C_{9-12}$)bicycloaryl($C_{0-3}$)alkyl or hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl or (iii) ($C_{3-6}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-6}$)cycloalkyl($C_{0-3}$)alkyl, phenyl($C_{0-3}$)alkyl or hetero($C_{5-6}$)aryl($C_{0-3}$)alkyl substituted by $-X^5OR^{15}$, $-X^5SR^{15}$, $-X^5S(O)R^{15}$, $-X^5S(O)_2R^{15}$, $-X^5C(O)R^{15}$, $-X^5C(O)OR^{15}$, $-X^5C(O)NR^{15}R^{16}$, $-X^5NR^{15}R^{16}$, $-X^5NR^{16}C(O)R^{15}$, $-X^5NR^{16}C(O)OR^{15}$, $-X^5NR^{16}C(O)NR^{15}R^{16}$ or $-X^5NR^{16}C(NR^{16})NR^{15}R^{16}$, wherein $X^5$ is a bond or methylene, $R^{15}$ is ($C_{3-6}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-6}$)cycloalkyl($C_{0-3}$)alkyl, phenyl($C_{0-3}$)alkyl or hetero($C_{5-6}$)aryl($C_{0-3}$)alkyl and $R^{16}$ is hydrogen or ($C_{1-6}$)alkyl; wherein $R^4$ optionally further contains 1 to 5 substituents which when occurring within an alicyclic or aromatic ring system are radicals independently selected from a group consisting of ($C_{1-6}$)alkyl, ($C_{1-6}$)alkylidene, cyano, halo, nitro, halo-substituted ($C_{1-3}$)alkyl, $-X^5NR^{17}R^{17}$, $-X^5NR^{17}C(O)OR^{17}$, $-X^5NR^{17}C(O)NR^{17}R^{17}$, $-X^5NR^{17}C(NR^{17})NR^{17}R^{17}$, $-X^5OR^{17}$, $-X^5SR^{17}$, $-X^5C(O)OR^{17}$, $-X^5C(O)NR^{17}R^{17}$, $-X^5S(O)_2NR^{17}R^{17}$, $-X^5P(O)(OR^8)OR^{17}$, $-X^5OP(O)(OR^8)OR^{17}$, $-X^5NR^{17}C(O)R^{18}$, $-X^5S(O)R^{18}$, $-X^5S(O)_2R^{18}$ and $-X^5C(O)R^{18}$ and when occurring within an aliphatic moiety are radicals independently selected from a group consisting of cyano, halo, nitro, $-NR^{17}R^{17}$, $-NR^{17}C(O)OR^{17}$, $-NR^{17}C(O)NR^{17}R^{17}$, $-NR^{17}C(NR^{17})NR^{17}R^{17}$, $-OR^{17}$, $-SR^{17}$, $-C(O)OR^{17}$, $-C(O)NR^{17}R^{17}$, $-S(O)_2NR^{17}R^{17}$, $-P(O)(OR^{17})OR^{17}$, $-OP(O)(OR^{17})OR^{17}$, $-NR^{17}C(O)R^{18}$, $-S(O)R^{18}$, $-S(O)_2R^{18}$ and $-C(O)R^{18}$, wherein $X^5$ is a bond or ($C_{1-6}$)alkylene, $R^{17}$ at each occurrence independently is hydrogen, ($C_{1-6}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{18}$ is ($C_{1-6}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates (e.g. hydrates) of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

A second aspect of the invention is a pharmaceutical composition which

contains a compound of Formula I or a *N*-oxide derivative, individual isomer or mixture of isomers thereof, or a pharmaceutically acceptable salt thereof, in admixture with one or more suitable excipients.

A third aspect of the invention is a method for treating a disease in an animal in which inhibition of cathepsin S can prevent, inhibit or ameliorate the pathology and/or symptomatology of the disease, which method comprises administering to the animal a therapeutically effective amount of compound of Formula I or a *N*-oxide derivative, individual isomer or mixture of isomers thereof; or a pharmaceutically acceptable salt thereof.

A fourth aspect of the invention is the processes for preparing compounds of Formula I and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and the pharmaceutically acceptable salts thereof.

## DETAILED DESCRIPTION OF THE INVENTION

Definitions:

Unless otherwise stated, the following terms used in the specification and claims are defined for the purposes of this Application and have the following meanings.

"Alicyclic" means a moiety characterized by arrangement of the carbon atoms in closed non-aromatic ring structures having properties resembling those of aliphatics and may be saturated or partially unsaturated with two or more double or triple bonds.

"Aliphatic" means a moiety characterized by a straight or branched chain arrangement of the constituent carbon atoms and may be saturated or partially unsaturated with two or more double or triple bonds.

"Alkyl" represented by itself means a straight or branched, saturated or unsaturated, aliphatic radical having the number of carbon atoms indicated (e.g., $(C_{1-6})$alkyl includes methyl, ethyl, propyl, isopropyl, butyl, *sec*-butyl, isobutyl, *tert*-butyl, vinyl, allyl, 1-propenyl, isopropenyl, 1-butenyl, 2-butenyl, 3-butenyl, 2-methylallyl, ethynyl, 1-propynyl, 2-propynyl, and the like). Alkyl represented along

with another radical (e.g., as in arylalkyl) means a straight or branched, saturated or unsaturated aliphatic divalent radical having the number of atoms indicated or when no atoms are indicated means a bond (e.g., $(C_{6-12})$aryl$(C_{0-3})$alkyl includes phenyl, benzyl, phenethyl, 1-phenylethyl 3-phenylpropyl, and the like).

"Alkylene", unless indicated otherwise, means a straight or branched, saturated or unsaturated, aliphatic, divalent radical having the number of carbon atoms indicated (e.g., $(C_{1-6})$alkylene includes methylene ($-CH_2-$), ethylene ($-CH_2CH_2-$), trimethylene ($-CH_2CH_2CH_2-$), tetramethylene ($-CH_2CH_2CH_2CH_2-$) 2-butenylene ($-CH_2CH=CHCH_2-$), 2-methyltetramethylene ($-CH_2CH(CH_3)CH_2CH_2-$), pentamethylene ($-CH_2CH_2CH_2CH_2CH_2-$) and the like).

"Alkenyl" means alkyl, as defined in this Application, provided that the radical is comprised of at least one double bond. Hence, optionally substituted $(C_{2-6})$alkenyl as used in this Application to define $R^3$ includes 2-bromovinyl (-CH=CHBr), buta-1,3-dienyl ($-CH=CH-CH=CH_2$), 2-chloro-1-methylpropenyl ($-C(CH_3)=CCl-CH_3$), 2-chlorovinyl (-CH=CHCl), 4-isopropenyl ($-C(CH_3)=CH_2$), 1-methylpropenyl ($-C(CH_3)=CH-CH_3$), 2-methylpropenyl ($-CH=C(CH_3)_2$), 2-nitrovinyl ($-CH=CHNO_2$), propenyl ($-CH=CH-CH_3$), 2-trifluoromethylvinyl ($-CH=CH-CF_3$), trifluorovinyl ($-CF=CF_2$), vinyl ($-CH=CH_2$), and the like).

"Alkylidene" means a straight or branched saturated or unsaturated, aliphatic, divalent radical having the number of carbon atoms indicated (e.g. $(C_{1-6})$alkylidene includes methylene ($=CH_2$), ethylidene ($=CHCH_3$), isopropylidene ($=C(CH_3)_2$), propylidene ($=CHCH_2CH_3$), allylidene ($=CH-CH=CH_2$), and the like).

"Amino" means the radical $-NH_2$. Unless indicated otherwise, the compounds of the invention containing amino moieties include protected derivatives thereof. Suitable protecting groups for amino moieties include acetyl, *tert*-butoxycarbonyl, benzyloxycarbonyl, and the like.

"Animal" includes humans, non-human mammals (e.g., dogs, cats, rabbits, cattle, horses, sheep, goats, swine, deer, and the like) and non-mammals (e.g., birds, and the like).

"Aromatic" means a moiety wherein the constituent atoms make up an unsaturated ring system, all atoms in the ring system are $sp^2$ hybridized and the total

number of pi electrons is equal to 4n+2.

"Aryl" means a monocyclic or bicyclic ring assembly (fused or linked by a single bond) containing the total number of ring carbon atoms indicated, wherein each ring is comprised of 6 ring carbon atoms and is aromatic or when fused with a second ring forms an aromatic ring assembly. For example, optionally substituted ($C_{6-12}$)aryl as used in this Application to define $R^3$ includes biphenyl-2-yl, 2-bromophenyl, 2-bromocarbonylphenyl, 2-bromo-5-fluorophenyl, 4-*tert*-butylphenyl, 4-carbamoylphenyl, 4-carboxy-2-nitrophenyl, 2-chlorophenyl, 4-chlorophenyl, 3-chlorocarbonylphenyl, 4-chlorocarbonylphenyl, 2-chloro-4-fluorophenyl, 2-chloro-6-fluorophenyl, 4-chloro-2-nitrophenyl, 6-chloro-2-nitrophenyl, 2,6-dibromophenyl, 2,3-dichlorophenyl, 2,5-dichlorophenyl, 3,4-dichlorophenyl, 2-difluoromethoxyphenyl, 3,5-dimethylphenyl, 2-ethoxycarbonylphenyl, 2-fluoropheny, 2-iodophenyl, 4-isopropylphenyl, 2-methoxyphenyl, 4-methoxyphenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 5-methyl-2-nitrophenyl, 4-methylsulfonylphenyl, naphth-2-yl, 2-nitrophenyl, 3-nitrophenyl, 4-nitrophenyl, 2,3,4,5,6-pentafluorophenyl, phenyl, 2-trifluoromethoxyphenyl, 3-trifluoromethoxyphenyl, 4-trifluoromethoxyphenyl, 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, 2-trifluoromethylsulfanylphenyl, 4-trifluoromethylsulfanylphenyl, and the like. Optionally substituted ($C_{6-12}$)aryl as used in this Application to define $R^4$ includes 3-acetylphenyl, 3-*tert*-butoxycarbonylaminomethylphenyl, biphenyl-4-yl, 3-hydroxyphenyl, 4-hydroxyphenyl, 3-methoxyphenyl, naphth-2-yl, 3-phenoxyphenyl, phenyl, and the like.

"Bicycloaryl" means a bicyclic ring assembly containing the number of ring carbon atoms indicated, wherein the rings are linked by a single bond or fused and one, but not both, of the rings comprising the assembly is aromatic, and any carbocyclic ketone, thioketone or iminoketone derivative thereof (e.g., ($C_{9-12}$)bicycloaryl includes cyclohexylphenyl, 1,2-dihydronaphthyl, 2,4-dioxo-1,2,3,4-tetrahydronaphthyl, indanyl, indenyl, phenylcyclohexyl, 1,2,3,4-tetrahydronaphthyl, and the like).

"Carbamoyl" means the radical $-C(O)NH_2$. Unless indicated otherwise, the compounds of the invention containing carbamoyl moieties include protected

derivatives thereof. Suitable protecting groups for carbamoyl moieties include acetyl, *tert*-butoxycarbonyl, benzyloxycarbonyl, and the like and both the unprotected and protected derivatives fall within the scope of the invention.

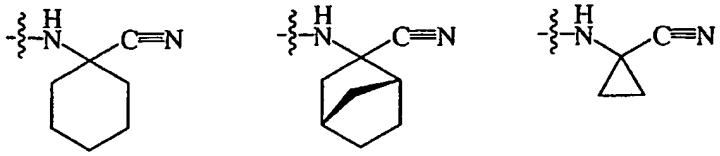
"Carbocyclic ketone derivative" means a derivative containing the moiety –C(O)–.

"Carboxy" means the radical -C(O)OH. Unless indicated otherwise, the compounds of the invention containing carboxy moieties include protected derivatives thereof. Suitable protecting groups for carboxy moieties include benzyl, *tert*-butyl, and the like.

"Cycloalkenyl" means cycloalkyl, as defined in this Application, provided that the ring assembly is comprised of at least one double bond. Hence, optionally substituted ($C_{5-12}$)cycloalkenyl as used in this Application to define $R^3$ includes cyclopent-1-enyl, 2-methylcyclopent-1-enyl, 2-nitrocyclopent-1-enyl, 2-fluorocyclopent-1-enyl, 2-chlorocyclopent-1-enyl, 2-trifluoromethylcyclopent-1-enyl, cyclohex-1-enyl, 2-methylcyclohex-1-enyl, 2-nitrocyclohex-1-enyl, 2-fluorocyclohex-1-enyl, 2-chlorocyclohex-1-enyl, 3-cyclohexa-1,3-dienyl, and the like).

"Cycloalkyl" means a saturated or partially unsaturated, monocyclic ring, bicyclic ring assembly (directly linked by a single bond or fused) or bridged polycyclic ring assembly containing the number of ring carbon atoms indicated, and any carbocyclic ketone, thioketone or iminoketone derivative thereof (e.g., ($C_{3-12}$)cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexenyl, 2,5-cyclohexadienyl, bicyclohexylyl, cyclopentylcyclohexyl, bicyclo[2.2.2]octyl, adamantan-1-yl, decahydronaphthyl, oxocyclohexyl, dioxocyclohexyl, thiocyclohexyl, 2-oxobicyclo[2.2.1]hept-1-yl, and the like).

"Cycloalkylene" means a divalent saturated or partially unsaturated, monocyclic ring or bridged polycyclic ring assembly containing the number of ring carbon atoms indicated, and any carbocyclic ketone, thioketone or iminoketone derivative thereof. For example, the instance wherein "$R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-8}$)cycloalkylene" includes, but is not limited to, the following:



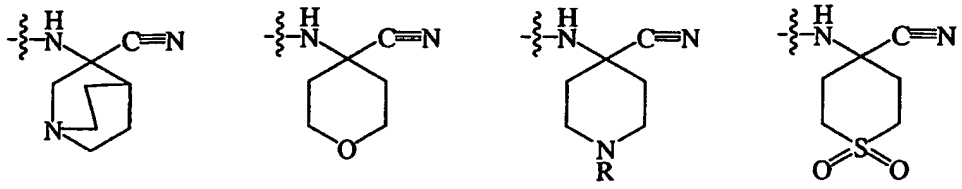
"Disease" specifically includes any unhealthy condition of an animal or part thereof and includes an unhealthy condition that may be caused by, or incident to, medical or veterinary therapy applied to that animal, i.e., the "side effects" of such therapy.

"Halo" means fluoro, chloro, bromo or iodo.

"Halo-substituted alkyl", as an isolated group or part of a larger group, means "alkyl" substituted by one or more "halo" atoms, as such terms are defined in this Application. Halo-substituted alkyl includes haloalkyl, dihaloalkyl, trihaloalkyl, perhaloalkyl and the like (e.g. halo-substituted $(C_{1-3})$alkyl includes chloromethyl, dichloromethyl, difluoromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, perfluoroethyl, 2,2,2-trifluoro-1,1-dichloroethyl, and the like).

"Heteroatom moiety" includes -N=, -NR-, -O-, -S- or $-S(O)_2-$, wherein R is hydrogen, $(C_{1-6})$alkyl or a protecting group.

"Heterocycloalkylene" means cycloalkylene, as defined in this Application, provided that one or more of the ring member carbon atoms indicated, is replaced by heteroatom moiety selected from -N=, -NR-, -O-, -S- or $-S(O)_2-$, wherein R is hydrogen or $(C_{1-6})$alkyl. For example, the instance wherein "$R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form hetero$(C_{3-8})$cycloalkylene" includes, but is not limited to, the following:



in which R is hydrogen, $(C_{1-6})$alkyl, or a protecting group.

"Heteroaryl" means aryl, as defined in this Application, provided that one or more of the ring carbon atoms indicated are replaced by a heteroatom moiety selected from -N=, -NR-, -O- or -S-, wherein R is hydrogen, ($C_{1-6}$)alkyl, a protecting group or represents the free valence which serves as the point of attachment to a ring nitrogen, and each ring is comprised of 5 or 6 ring atoms. For example, optionally substituted hetero($C_{5-12}$)aryl as used in this Application to define $R^3$ includes 4-amino-2-hydroxypyrimidin-5-yl, benzothiazol-2-yl, 1*H*-benzoimidazol-2-yl, 2-bromopyrid-5-yl, 5-bromopyrid-2-yl, 4-carbamoylthiazol-2-yl, 3-carboxypyrid-4-yl, 5-carboxy-2,6-dimethylpyrid-3-yl, 3,5-dimethylisoxazol-4-yl, 5-ethoxy-2,6-dimethylpyrid-3-yl, 5-fluoro-6-hydroxypyrimidin-4-yl, fur-2-yl, fur-3-yl, 5-hydroxy-4,6-dimethylpyrid-3-yl, 8-hydroxy-5,7-dimethylquinolin-2-yl, 5-hydroxymethylisoxazol-3-yl, 3-hydroxy-6-methylpyrid-2-yl, 3-hydroxypyrid-2-yl, 1*H*-imidazol-2-yl, 1*H*-imidazol-4-yl, 1*H*-indol-3-yl, isothiazol-4-yl, isoxazol-4-yl, 2-methylfur-3-yl, 5-methylfur-2-yl, 1-methyl-1*H*-imidazol-2-yl, 5-methyl-3*H*-imidazol-4-yl, 5-methylisoxazol-3-yl, 5-methyl-2*H*-pyrazol-3-yl, 3-methylpyrid-2-yl, 4-methylpyrid-2-yl, 5-methylpyrid-2-yl, 6-methylpyrid-2-yl, 2-methylpyrid-3-yl, 2-methylthiazol-4-yl, 5-nitropyrid-2-yl, 2*H*-pyrazol-3-yl, 3*H*-pyrazol-4-yl, pyridazin-3-yl, pyrid-2-yl, pyrid-3-yl, pyrid-4-yl, 5-pyrid-3-yl-2*H*-[1,2,4]triazol-3-yl, pyrimidin-4-yl, pyrimidin-5-yl, 1*H*-pyrrol-3-yl, quinolin-2-yl, 1*H*-tetrazol-5-yl, thiazol-2-yl, thiazol-5-yl, thien-2-yl, thien-3-yl, 2*H*-[1,2,4]triazol-3-yl, 3*H*-[1,2,3]triazol-4-yl, 5-trifluoromethylpyrid-2-yl, and the like. Suitable protecting groups include *tert*-butoxycarbonyl, benzyloxycarbonyl, benzyl, 4-methoxybenzyl, 2-nitrobenzyl, and the like. Optionally substituted hetero($C_{5-12}$)aryl as used in this Application to define $R^4$ includes benzofur-2-yl, fur-2-yl, fur-3-yl, pyrid-3-yl, pyrid-4-yl, quinol-2-yl, quinol-3-yl, thien-2-yl, thien-3-yl, and the like.

"Heterobicycloaryl" means bicycloaryl, as defined in this Application, provided that one or more of the ring carbon atoms indicated are replaced by a heteroatom moiety selected from -N=, -NR-, -O- or -S-, wherein R is hydrogen, ($C_{1-6}$)alkyl, a protecting group or represents the free valence which serves as the point of attachment to a ring nitrogen, and any carbocyclic ketone, thioketone or iminoketone derivative thereof. For example, optionally substituted hetero($C_{8-12}$)bicycloaryl as used in this Application to

define $R^3$ includes 2-amino-4-oxo-3,4-dihydropteridin-6-yl, and the like. In general, the term heterobicycloaryl as used in this Application includes, for example, benzo[1,3]dioxol-5-ylcarbonyl, 3,4-dihydro-2*H*-[1,8]naphthyridinyl, 3,4-dihydro-2*H*-quinolinyl, 2,4-dioxo-3,4-dihydro-2*H*-quinazolinyl, 1,2,3,4,5,6-hexahydro[2,2']bipyridinylyl, morpholinylpyridyl, 3-oxo-2,3-dihydrobenzo[1,4]oxazinyl, piperidinylphenyl, 5,6,7,8-tetrahydroquinolinyl, and the like. For example, hetero($C_{5-12}$)aryl as used in this Application to define $R^4$ includes benzo[1,3]dioxol-5-yl. For example, hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl used to describe $R^{11}$ in this Application, includes 1-oxo-1,3-dihydroisoindol-2-yl, quinolin-3-yl, quinolin-2-yl, 3a,7a-dihydrobenzo[1,3]dioxol-5-yl, naphthalen-2-yl, 3-chlorobenzo[*b*]thiophen-2-yl, benzo[*b*]thiophen-2-yl and 1*H*-indol-5-yl, and the like.

"Heterocycloalkenyl" means heterocycloalkyl, as defined in this Application, provided that the ring assembly is comprised of at least one double bond. Hence, optionally substituted hetero($C_{5-12}$)cycloalkenyl as used in this Application to define $R^3$ includes 2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl, 2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl, 5-hydroxy-4-oxo-4*H*-pyran-2-yl, 5-methoxy-4-oxo-4*H*-pyran-2-yl, 6-oxo-1,6-dihydropyrimidin-5-yl, 4-oxo-1,4-dihydropyrid-2-yl, 6-oxo-1,6-dihydropyrid-2-yl, 6-oxo-1,6-dihydropyrid-3-yl, and the like).

"Heterocycloalkyl" means cycloalkyl, as defined in this Application, provided that one or more of the ring carbon atoms indicated are replaced by a heteroatom moiety selected from -N=, -NR-, -O- or -S-, wherein R is hydrogen, ($C_{1-6}$)alkyl, a protecting group or represents the free valence which serves as the point of attachment to a ring nitrogen, and any carbocyclic ketone, thioketone or iminoketone derivative thereof (e.g., the term hetero($C_{5-12}$)cycloalkyl includes [1,4']bipiperidinylyl, 1',2'-dihydro-2*H*-[1,4']bipyridinylyl, imidazolidinyl, morpholinyl, 1-morpholin-4-ylpiperidinyl, piperazinyl, piperidyl, pyrrolidinyl, pyrrolinyl, quinuclidinyl, and the like). Thus, for example, optionally substituted hetero($C_{5-12}$)cycloalkyl as used in this Application to define $R^4$ includes 4-*tert*-butoxycarbonylpiperazin-1-yl, 4-ethoxycarbonylpiperazin-1-yl, 4-fur-2-ylcarbonylpiperazin-1-yl, morpholin-4-yl, and the like. Suitable protecting groups include *tert*-butoxycarbonyl, benzyloxycarbonyl, benzyl, 4-methoxybenzyl, 2-nitrobenzyl, and the like. For example, a compound of

Formula I wherein $R^4$ is piperidin-4-ylcarbonyl may exist as either the unprotected or a protected derivative, e.g., wherein $R^4$ is 4-*tert*-butoxycarbonylpiperazin-1-ylcarbonyl, and both the unprotected and protected derivatives fall within the scope of the invention.

"Hydroxy" means the radical -OH. Unless indicated otherwise, the compounds of the invention containing hydroxy radicals include protected derivatives thereof. Suitable protecting groups for hydroxy moieties include benzyl and the like.

"Iminoketone derivative" means a derivative containing the moiety -C(NR)-, wherein R is hydrogen or $(C_{1-6})$alkyl.

"Isomers" mean compounds of Formula I having identical molecular formulae but differ in the nature or sequence of bonding of their atoms or in the arrangement of their atoms in space. Isomers that differ in the arrangement of their atoms in space are termed "stereoisomers". Stereoisomers that are not mirror images of one another are termed "diastereomers" and stereoisomers that are nonsuperimposable mirror images are termed "enantiomers" or sometimes "optical isomers". A carbon atom bonded to four nonidentical substituents is termed a "chiral center". A compound with one chiral center has two enantiomeric forms of opposite chirality is termed a "racemic mixture". A compound that has more than one chiral center has $2^{n-1}$ enantiomeric pairs, where $n$ is the number of chiral centers. Compounds with more than one chiral center may exist as ether an individual diastereomers or as a mixture of diastereomers, termed a "diastereomeric mixture". When one chiral center is present a stereoisomer may be characterized by the absolute configuration of that chiral center. Absolute configuration refers to the arrangement in space of the substituents attached to the chiral center. Enantiomers are characterized by the absolute configuration of their chiral centers and described by the *R*- and *S*-sequencing rules of Cahn, Ingold and Prelog. Conventions for stereochemical nomenclature, methods for the determination of stereochemistry and the separation of stereoisomers are well known in the art (e.g., see "Advanced Organic Chemistry", 4th edition, March, Jerry, John Wiley & Sons, New York, 1992). It is understood that the names and illustration used in this Application to describe compounds of Formula I are meant to be encompassed all possible stereoisomers. Thus, for example, the name *N*-[1-cyanomethylcarbamoyl-2-(3,4-

difluorobenzylsulfonyl)ethyl]benzamide is meant to include *N*-[1-*R*-cyanomethylcarbamoyl-2-(3,4-difluorobenzylsulfonyl)ethyl]benzamide and *N*-[1-*S*-cyanomethylcarbamoyl-2-(3,4-difluorobenzylsulfonyl)ethyl]benzamide and any mixture, racemic or otherwise, thereof.

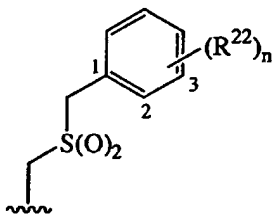
"Ketone derivative" means a derivative containing the moiety -C(O)-.

"Methylene" means the divalent radical $-CH_2-$.

"Nitro" means the radical $-NO_2$.

"Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not. For example, the phrase "$R^3$ optionally is substituted by 1 to 5 radicals" means that $R^3$ may or may not be substituted in order to fall within the scope of the invention.

"Ortho" and "meta" have the meaning typically associated with their usage in organic chemistry. Hence, the phrase "$R^{22}$ at the first occurrence is attached at the ring carbon ortho or meta to the 1-position of the phenyl moiety", refers to the following illustrative example:




wherein $R^{22}$ is attached at the 2 or 3-position.

"*N*-oxide derivatives" means derivatives of compounds of Formula I in which nitrogens are in an oxidized state (i.e., O-N) and which possess the desired pharmacological activity.

"Pathology" of a disease means the essential nature, causes and development of the disease as well as the structural and functional changes that result from the disease processes.

"Pharmaceutically acceptable" means that which is useful in preparing a pharmaceutical composition that is generally safe, non-toxic and neither biologically

nor otherwise undesirable and includes that which is acceptable for veterinary use as well as human pharmaceutical use.

"Pharmaceutically acceptable salts" means salts of compounds of Formula I which are pharmaceutically acceptable, as defined above, and which possess the desired pharmacological activity. Such salts include acid addition salts formed with inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, phosphoric acid, and the like; or with organic acids such as acetic acid, propionic acid, hexanoic acid, heptanoic acid, cyclopentanepropionic acid, glycolic acid, pyruvic acid, lactic acid, malonic acid, succinic acid, malic acid, maleic acid, fumaric acid, tartatic acid, citric acid, benzoic acid, *o*-(4-hydroxybenzoyl)benzoic acid, cinnamic acid, madelic acid, methanesulfonic acid, ethanesulfonic acid, 1,2-ethanedisulfonic acid, 2-hydroxyethanesulfonic acid, benzenesulfonic acid, *p*-chlorobenzenesulfonic acid, 2-naphthalenesulfonic acid, *p*-toluenesulfonic acid, camphorsulfonic acid, 4-methylbicyclo[2.2.2]oct-2-ene-1-carboxylic acid, glucoheptonic acid, 4,4'-methylenebis(3-hydroxy-2-ene-1-carboxylic acid), 3-phenylpropionic acid, trimethylacetic acid, tertiary butylacetic acid, lauryl sulfuric acid, gluconic acid, glutamic acid, hydroxynaphthoic acid, salicylic acid, stearic acid, muconic acid and the like.

Pharmaceutically acceptable salts also include base addition salts which may be formed when acidic protons present are capable of reacting with inorganic or organic bases. Acceptable inorganic bases include sodium hydroxide, sodium carbonate, potassium hydroxide, aluminum hydroxide and calcium hydroxide. Acceptable organic bases include ethanolamine, diethanolamine, triethanolamine, tromethamine, *N*-methylglucamine and the like.

"Prodrug" means a compound which is convertible in vivo by metabolic means (e.g. by hydrolysis) to a compound of Formula I. For example an ester of a compound of Formula I containing a hydroxy group may be convertible by hydrolysis in vivo to the parent molecule. Alternatively an ester of a compound of Formula I containing a carboxy group may be convertible by hydrolysis in vivo to the parent molecule. Suitable esters of compounds of Formula I containing a hydroxy group, are for example acetates, citrates, lactates, tartrates, malonates, oxalates, salicylates, propionates,

succinates, fumarates, maleates, methylene-bis-b-hydroxynaphthoates, gentisates, isethionates, di-*p*-toluoyltartrates, methanesulphonates, ethanesulphonates, benzenesulphonates, p-toluenesulphonates, cyclohexylsulphamates and quinates. Suitable esters of compounds of Formula I containing a carboxy group, are for example those described by F.J.Leinweber, Drug Metab. Res., 1987, 18, page 379. An especially useful class of esters of compounds of Formula I containing a hydroxy group, may be formed from acid moieties selected from those described by Bundgaard et al., J. Med. Chem., 1989, 32, page 2503-2507, and include substituted (aminomethyl)-benzoates, for example, dialkylamino-methylbenzoates in which the two alkyl groups may be joined together and/or interrupted by an oxygen atom or by an optionally substituted nitrogen atom, e.g. an alkylated nitrogen atom, more especially (morpholino-methyl)benzoates, e.g. 3- or 4-(morpholinomethyl)-benzoates, and (4-alkylpiperazin-1-yl)benzoates, e.g. 3- or 4-(4-alkylpiperazin-1-yl)benzoates.

"Protected derivatives" means derivatives of compounds of Formula I in which a reactive site or sites are blocked with protecting groups. Protected derivatives of compounds of Formula I are useful in the preparation of compounds of Formula I or in themselves may be active cathepsin S inhibitors. A comprehensive list of suitable protecting groups can be found in T.W. Greene, *Protecting Groups in Organic Synthesis*, 3rd edition, John Wiley & Sons, Inc. 1999.

"Therapeutically effective amount" means that amount which, when administered to an animal for treating a disease, is sufficient to effect such treatment for the disease.

"Thioketone derivative" means a derivative containing the moiety -C(S)-.

"Treatment" or "treating" means any administration of a compound of the present invention and includes:

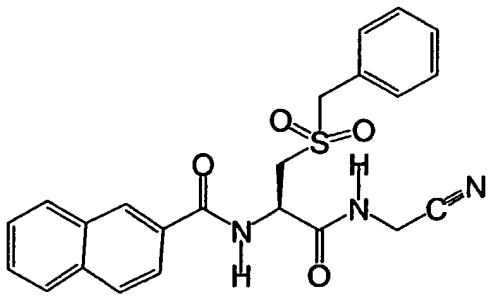
(1) preventing the disease from occurring in an animal which may be predisposed to the disease but does not yet experience or display the pathology or symptomatology of the disease,

(2) inhibiting the disease in an animal that is experiencing or displaying the pathology or symptomatology of the diseased (i.e., arresting further development of the pathology and/or symptomatology), or

(3) ameliorating the disease in an animal that is experiencing or displaying the pathology or symptomatology of the diseased (i.e., reversing the pathology and/or symptomatology).

Nomenclature:

The compounds of Formula I and the intermediates and starting materials used in their preparation are named in accordance with IUPAC rules of nomenclature in which the characteristic groups have decreasing priority for citation as the principle group as follows: acids, esters, amides, etc. Alternatively, the compounds are named by AutoNom 4.0 (Beilstein Information Systems, Inc.). For example, a compound of Formula I in which $R^1$ and $R^2$ are each hydrogen, $R^3$ is phenyl, $X^2$ is methylene and $R^4$ is naphthalen-2-yl-methanoyl; that is, a compound having the following structure:



is named *N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)naphthalene-2-carboxamide or naphthalene-2-carboxylic acid [(R)-1-(cyanomethyl-carbamoyl)-2-phenylmethanesulfonyl-ethyl]-amide;

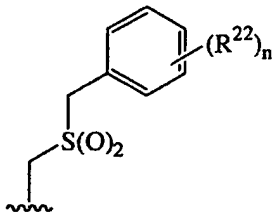
Presently Preferred Embodiments:

While the broadest definition of the invention is set forth in the Summary of the Invention, certain aspects of the invention are preferred. For example, $R^1$ particularly represents hydrogen and $R^2$ represents hydrogen, hetero($C_5$)aryl or ($C_{1-4}$)alkyl-substituted hetero($C_5$)aryl or $R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-5}$)cycloalkylene or ($C_{5-6}$)heterocycloalkylene.

Preferably $X^1$ and $X^2$ are both methylene and $R^3$ represents $(C_{2-6})$alkenyl, $(C_{6-12})$aryl or hetero$(C_{5-12})$aryl, each optionally substituted by 1 to 5 radicals selected from a group consisting of $(C_{1-4})$alkyl, cyano, halo, halo-substituted $(C_{1-4})$alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or $(C_{1-2})$alkylene, $R^9$ at each occurrence independently is hydrogen, $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl and $R^{10}$ is $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl. $R^3$ more preferably represents biphenyl, isooxazolyl, naphthyl, phenyl, pyridyl, thienyl or vinyl, each optionally substituted by 1 to 5 radicals selected from a group consisting of $(C_{1-4})$alkyl, cyano, halo, halo-substituted $(C_{1-4})$alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or $(C_{1-2})$alkylene, $R^9$ at each occurrence independently is hydrogen, $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl and $R^{10}$ is $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl. $R^3$ more preferably represents biphenyl-2-yl, 2,4-bistrifluoromethylphenyl, 2,5-bistrifluoromethylphenyl, 4-*tert*-butylphenyl, 2-bromophenyl, 3-bromophenyl, 4-bromophenyl, 2-bromo-5-fluorophenyl, 3-chloro-2-fluorophenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 5-chlorothien-2-yl, 2-chloro-5-trifluoromethyl, 2-cyanophenyl, 3-cyanophenyl, 4-cyanophenyl, 1,5-dichlorophenyl, 2,6-dichlorophenyl, 3,4-dichlorophenyl, 2,3-difluorophenyl, 2,4-difluorophenyl, 3,4-difluorophenyl, 2-difluoromethoxyphenyl, 3-difluoromethoxyphenyl, 4-difluoromethoxyphenyl, 2,5-difluorophenyl, 2,6-difluorophenyl, 3,5-dimethylisooxaxol-4-yl, 3,5-dimethylphenyl, 2-fluoro-6-nitrophenyl, 2-fluorophenyl, 4-fluorophenyl, 2-fluoro-3-trifluoromethylphenyl, 2-fluoro-4-trifluoromethylphenyl, 2-fluoro-5-trifluoromethylphenyl, 2-fluoro-6-trifluoromethylphenyl, 4-fluoro-2-trifluoromethylphenyl, 4-fluoro-3-trifluoromethylphenyl, 2-iodophenyl, 3-iodophenyl, 4-iodophenyl, 2-methoxyphenyl, 4-methoxyphenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 3-methyl-2-fluorophenyl, naphth-2-yl, 2-nitrophenyl, 3-nitrophenyl, 4-nitrophenyl, 2,3,4,5,6-pentafluorophenyl, phenyl, prop-2-en-1-yl, pyrid-2-yl, pyrid-3-yl, pyrid-4-yl, 2-trifluoromethoxyphenyl, 3-trifluoromethoxyphenyl, 4-trifluoromethoxyphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, 2-trifluoromethylsulfanylphenyl, 3-trifluoromethylsulfanylphenyl,

4-trifluoromethylsulfanylphenyl, 2,3,4-trifluorophenyl, 2,3,5-trifluorophenyl, 2,4,6-trifluorophenyl, 2,4,5-trifluorophenyl or 2,3,6-trifluorophenyl.

In particular, $X^1$, $X^2$ and $R^3$ along with the sulfonyl moiety to which $X^1$ and $X^2$ are attached together represent a group having the following formula:

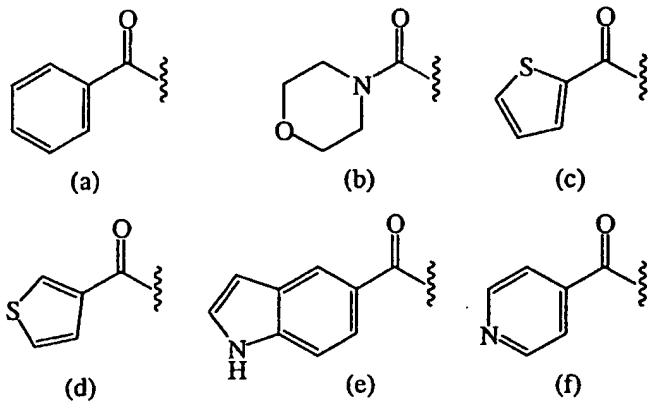



in which n is 0, 1, 2, 4 or 5 and $R^{22}$ at each occurrence independently is selected from a group consisting of $(C_{1-4})$alkyl, cyano, halo, halo-substituted $(C_{1-4})$alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or $(C_{1-2})$alkylene, $R^9$ at each occurrence independently is hydrogen, $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl and $R^{10}$ is $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl; more particularly in which n is 0, 1 or 2 and $R^{22}$ at each occurrence independently is selected from a group consisting of $(C_{1-4})$alkyl, cyano, halo, halo-substituted $(C_{1-4})$alkyl, nitro, $-OR^9$, $-SR^9$ and $-C(O)OR^9$, wherein $R^9$ at each occurrence independently is hydrogen, $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl; more particularly in which $R^{22}$ at each occurrence independently is selected from a group consisting of $(C_{1-4})$alkyl, bromo, carboxy, chloro, cyano, difluoromethoxy, fluoro, iodo, methoxy, nitro, trifluoromethoxy, trifluoromethyl and trifluorosulfanyl; more particularly in which at the first occurrence is attached at the ring carbon ortho or meta to the 1-position of the phenyl moiety.

$R^4$ preferably may represent $-C(O)X^4R^{11}$ or $-S(O)_2X^4R^{11}$, wherein $X^4$ is a bond, -O- or $-NR^{12}-$, wherein $R^{12}$ is hydrogen or $(C_{1-6})$alkyl, and $R^{11}$ is $(C_{1-6})$alkyl, $(C_{3-12})$cycloalkyl$(C_{0-3})$alkyl, hetero$(C_{5-12})$cycloalkyl$(C_{0-3})$alkyl, $(C_{6-10})$aryl$(C_{0-3})$alkyl, hetero$(C_{5-10})$aryl$(C_{0-3})$alkyl, hetero$(C_{8-12})$bicycloaryl$(C_{0-3})$alkyl, hetero$(C_{5-6})$cycloalkyl$(C_{0-3})$alkyl or phenyl$(C_{0-3})$alkyl, wherein the hetero$(C_{5-6})$cycloalkyl or phenyl is substituted in the ring by $-X^5OR^{15}$ or $-X^5C(O)R^{15}$,

wherein $X^5$ is a bond or methylene and $R^{15}$ is phenyl($C_{0-3}$)alkyl or hetero($C_{5-6}$)aryl($C_{0-3}$)alkyl, wherein any aryl or heteroaryl group comprising $R^4$ optionally is substituted in the ring by 1 to 2 substituents selected from ($C_{1-6}$)alkyl, halo, halo-substituted ($C_{1-3}$)alkyl, $-X^5OR^{17}$, $-X^5NR^{17}C(O)OR^{17}$, $-X^5C(O)OR^{17}$ or $-X^5C(O)R^{18}$, wherein $X^5$ is a bond or ($C_{1-6}$)alkylene, $R^{17}$ is hydrogen, ($C_{1-6}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{18}$ is ($C_{1-6}$)alkyl or halo-substituted ($C_{1-3}$)alkyl. $R^4$ more preferably may represent 3-acetylbenzoyl, allyloxycarbonyl, 2-aminopyrid-3-ylcarbonyl, 6-aminopyrid-3-ylcarbonyl, benzo[1,3]dioxol-5-ylcarbonyl, benzoyl, 4-benzoylbenzoylcarbonyl, benzo[1,3]dioxol-3-ylcarbonyl, benzofur-2-ylcarbonyl, biphenyl-4-ylcarbonyl, 4-bromobenzoyl, 3-bromothien-2-yl, *tert*-butoxycarbonyl, 3-*tert*-butoxycarbonylaminomethylbenzoyl, 4-*tert*-butoxycarbonylpiperazin-1-ylcarbonyl, 3-chlorobenzoyl, 4-chlorobenzoyl, 3-chlorothienylcarbonyl, cyclopentylcarbonyl, 3,4-difluorobenzoyl, 3,4-dimethoxybenzoyl, dimethylcarbamoyl, 4-ethoxycarbonylpiperazin-1-ylcarbonyl, 4-fluorobenzoyl, 3-fluoro-4-methoxybenzoyl, fur-2-ylcarbonyl, fur-3-ylcarbonyl, 4-fur-2-ylcarbonylpiperazin-1-ylcarbonyl, 3-hydroxybenzoyl, 4-hydroxybenzoyl, 4-hydroxypyrid-3-yl, 6-hydroxypyrid-3-yl, 1*H*-indol-4-ylcarbonyl, isopropylcarbamoyl, isobutyloxycarbonyl, isopropyloxycarbonyl, 3-methoxybenzoyl, 4-methoxybenzoyl, 3-methylbenzoyl, 5-methylthienylcarbonyl, 4-methylvaleryl, morpholin-4-ylcarbonyl, naphth-2-ylcarbonyl, naphth-2-ylsulfonyl, 3-phenoxybenzoyl, 3-phenylacryloyl, phenylsulfonyl, pyrazin-2-ylcarbonyl, 3-pyrid-3-ylacryl, pyrid-2-ylcarbonyl, pyrid-3-ylcarbonyl, pyrid-4-ylcarbonyl, quinol-2-ylcarbonyl, quinol-3-ylcarbonyl, thien-2-ylcarbonyl, thien-3-ylcarbonyl, thien-2-ylsulfonyl, 4-trifluoromethoxybenzoyl or 4-trifluoromethylbenzoyl.

$R^4$ more preferably is benzoyl, morpholin-4-ylcarbonyl, thienylcarbonyl, indolylcarbonyl or pyridinylcarbonyl, optionally substituted in the ring by 1 to 2 substituents selected from fluoro and methyl. In particular, $R^4$ represents one of the following formulae:




namely benzoyl, morpholin-4-ylcarbonyl, thien-2-yl, thien-3-yl, indol-4-yl and pyridin--4-yl, respectively, optionally substituted in the ring by 1 to 2 substituents selected from fluoro and methyl.

Reference to the preferred embodiments set forth above is meant to include all combinations of particular and preferred groups.

Particular compounds of the invention are selected from the compounds formed by joining the acyl carbon atom (C*) of one of the fragments (A1 to A36 or A40 to A71) shown in Table 1 to the nitrogen atom (N*) of one of the substituted aminoalkyl fragments (B1 to B75) shown in Table 2, and joining the methine carbon atom (CH*) of one of the substituted aminoalkyl fragments (B1 to B75) shown in Table 2 to the acyl carbon atom (C*) of one of the acyl-aminoalkylnitrile fragments(C1 to C9) depicted in Table 3.

Further particular compounds of the invention are selected from the compounds formed by joining the sulphonyl atom ($SO_2$*) of one of the fragments (A37 to A39) shown in Table 1 to the nitrogen atom (N*) of one of the substituted aminoalkyl fragments (B1 to B75) shown in Table 2, and joining the methine carbon atom (CH*) of one of the substituted aminoalkyl fragments (B1 to B75) shown in Table 2 to the acyl carbon atom (C*) of one of the acyl-aminoalkylnitrile fragments(C1 to C9) depicted in Table 3.

TABLE 1

| | | | | | |
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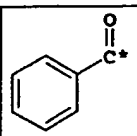
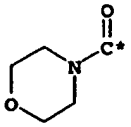
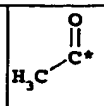
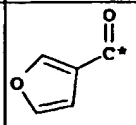
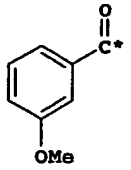
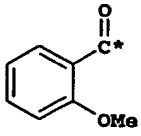
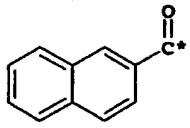
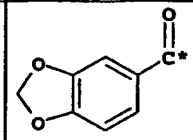
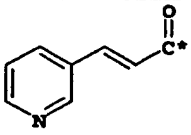
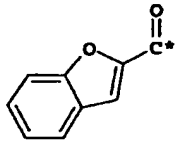
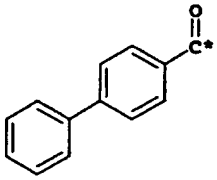
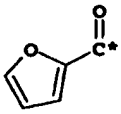
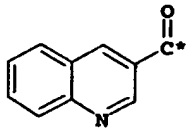
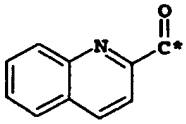
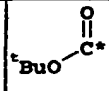
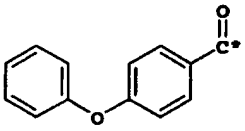
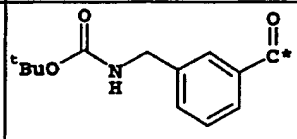
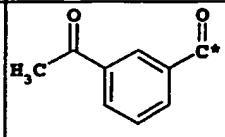
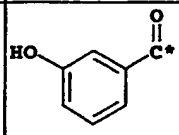
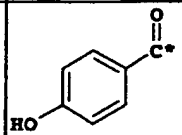
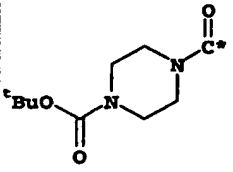
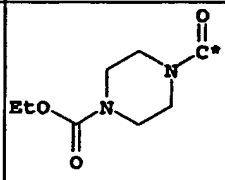
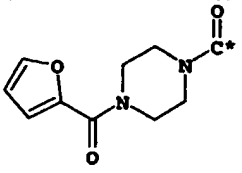
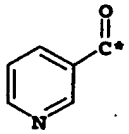
| A1 |  | A2 |  | A3 |  |
| A4 |  | A5 |  | A6 |  |
| A7 |  | A8 |  | A9 |  |
| A10 |  | A11 |  | A12 |  |
| A13 |  | A14 |  | A15 |  |
| A16 |  | A17 |  | A18 |  |
| A19 |  | A20 |  | A21 |  |
| A22 |  | A23 |  | A24 |  |

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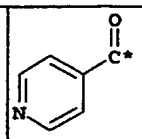
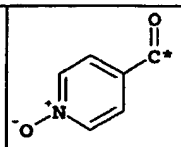
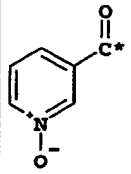
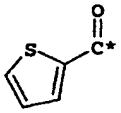
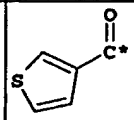
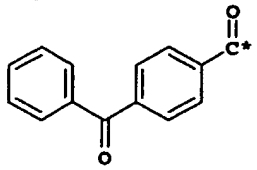
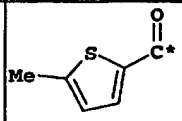
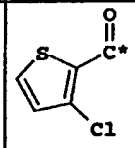
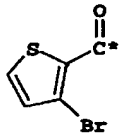
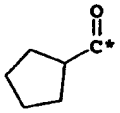
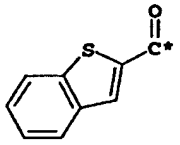
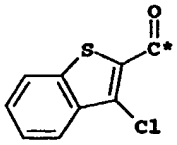
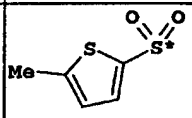
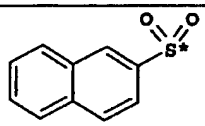
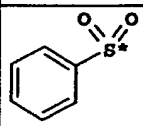
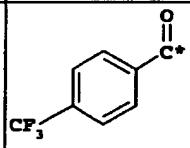
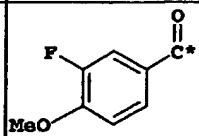
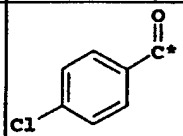
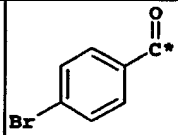
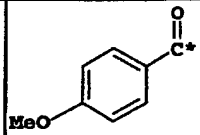
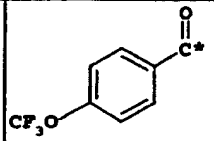
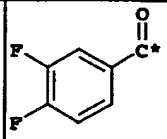
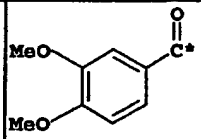
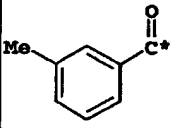
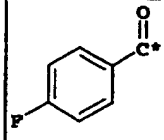
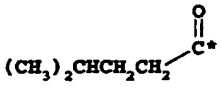
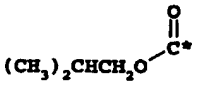
| A25 |  | A26 |  | A27 |  |
| A28 |  | A29 |  | A30 |  |
| A31 |  | A32 |  | A33 |  |
| A34 |  | A35 |  | A36 |  |
| A37 |  | A38 |  | A39 |  |
| A40 |  | A41 |  | A42 |  |
| A43 |  | A44 |  | A45 |  |
| A46 |  | A47 |  | A48 |  |
| A49 |  | A50 |  | A51 |  |

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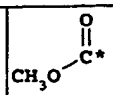
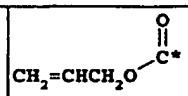
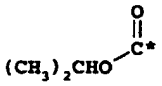
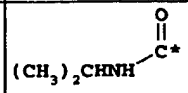
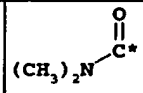
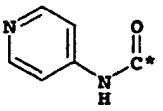
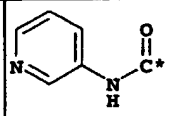
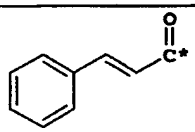
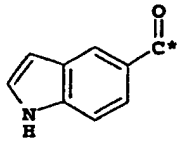
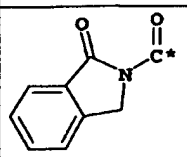
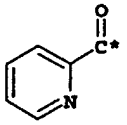
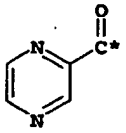
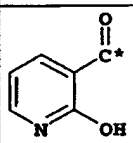
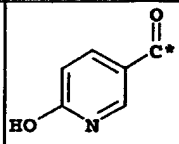
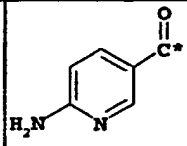
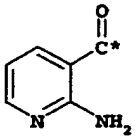
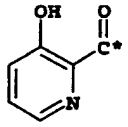
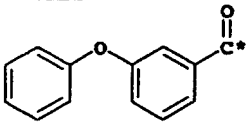
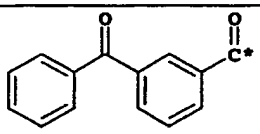
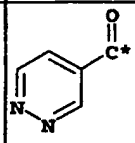
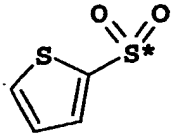
| A52 |  | A53 |  | A54 |  |
| A55 |  | A56 |  | A57 |  |
| A58 |  | A59 |  | A60 |  |
| A61 |  | A62 |  | A63 |  |
| A64 |  | A65 |  | A66 |  |
| A67 |  | A68 |  | A69 |  |
| A70 |  | A71 |  | A72 |  |

## TABLE 2

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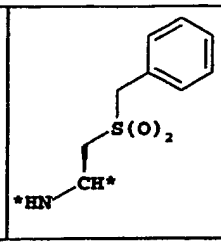
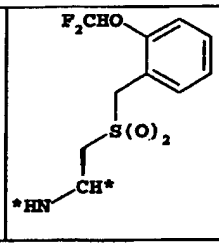
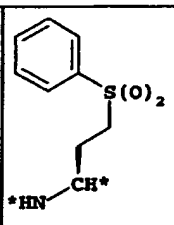
| B1 |  | B2 |  | B3 |  |

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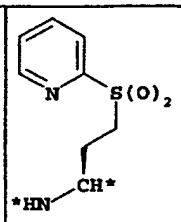
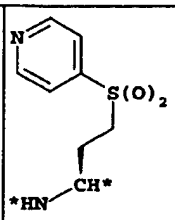
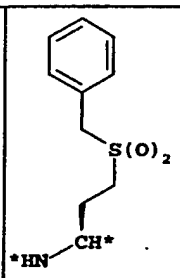
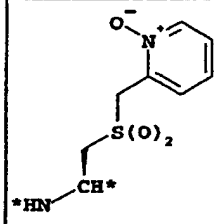
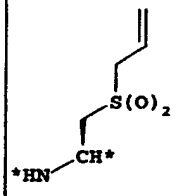
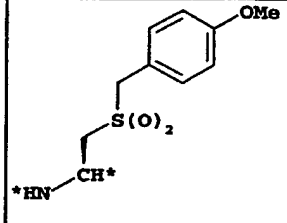
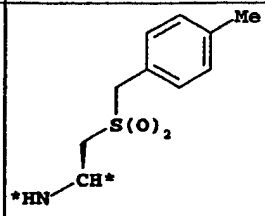
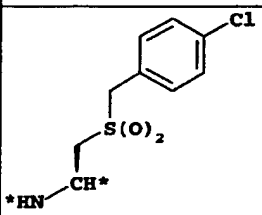
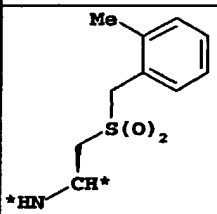
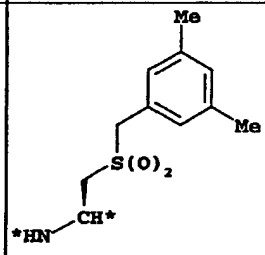
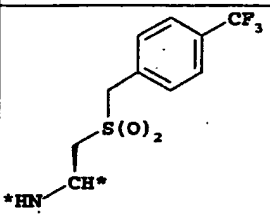
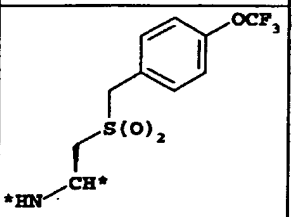
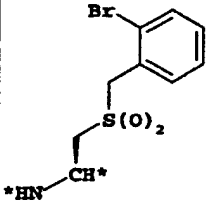
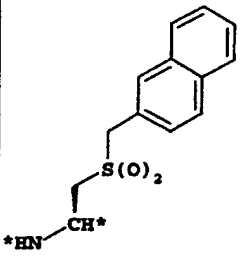
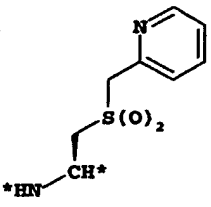
| B4 |  | B5 |  | B6 |  |
| B7 |  | B8 |  | B9 |  |
| B10 |  | B11 |  | B12 |  |
| B13 |  | B14 |  | B15 |  |
| B16 |  | B17 |  | B18 |  |

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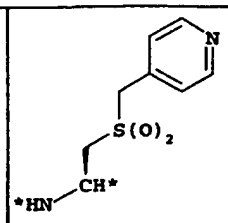
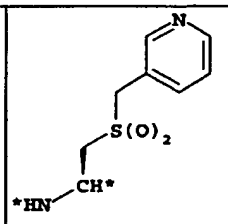
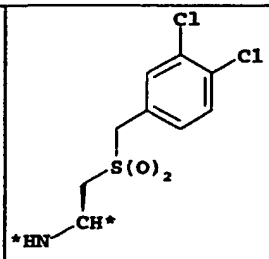
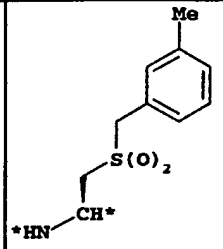
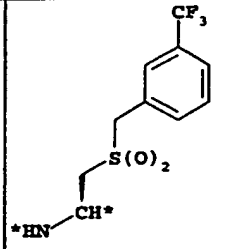
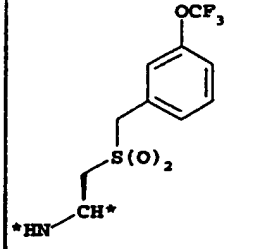
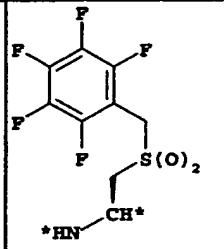
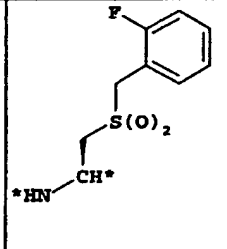
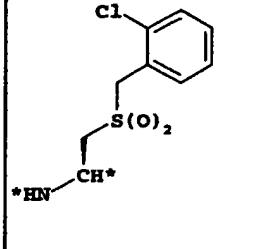
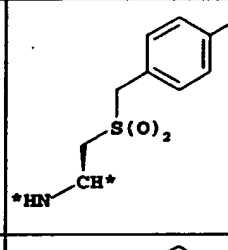
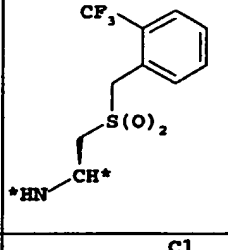
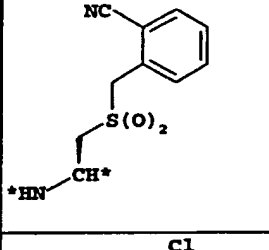
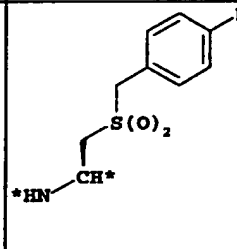
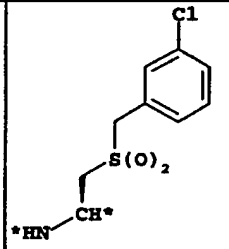
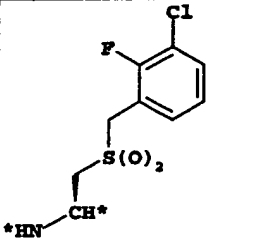
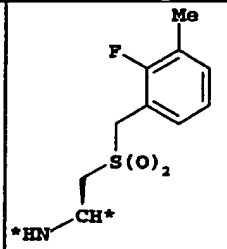
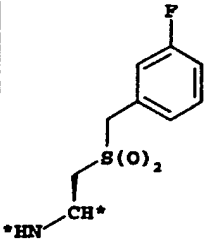
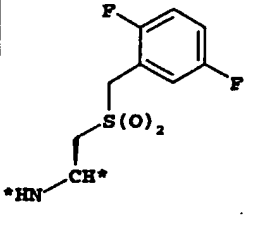
| B19 |  | B20 |  | B21 |  |
| B22 |  | B23 |  | B24 |  |
| B25 |  | B26 |  | B27 |  |
| B28 |  | B29 |  | B30 |  |
| B31 |  | B32 |  | B33 |  |
| B34 |  | B35 |  | B36 |  |

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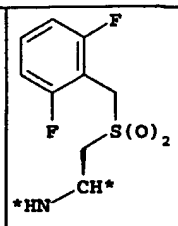
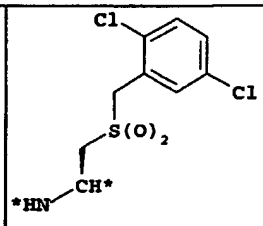
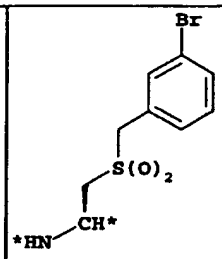
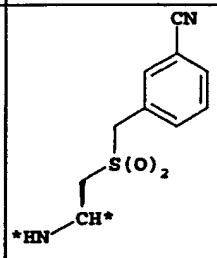
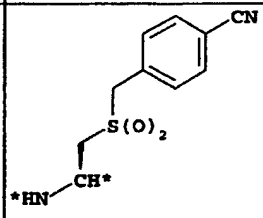
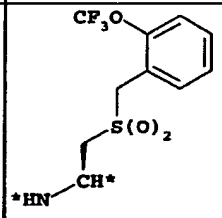
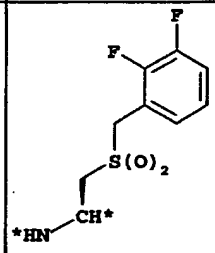
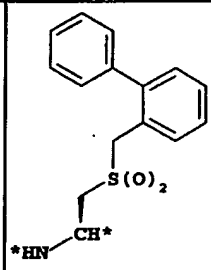
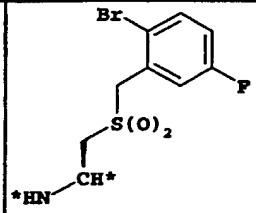
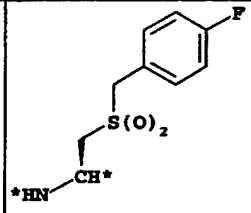
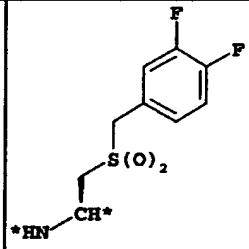
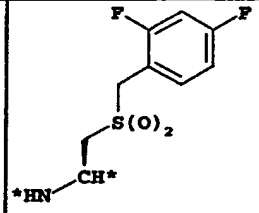
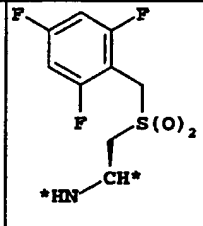
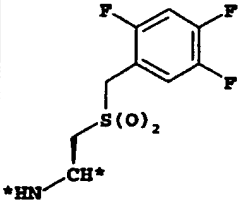
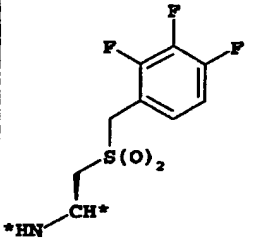
| B37 |  | B38 |  | B39 |  |
| B40 |  | B41 |  | B42 |  |
| B43 |  | B44 |  | B45 |  |
| B46 |  | B47 |  | B48 |  |
| B49 |  | B50 |  | B51 |  |

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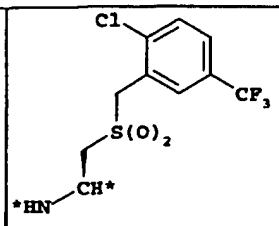
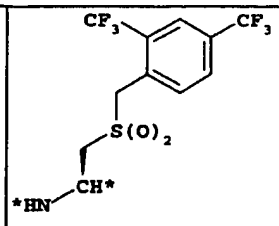
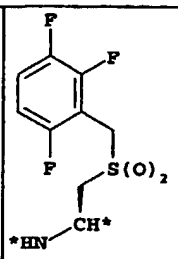
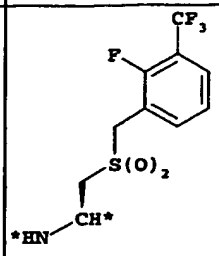
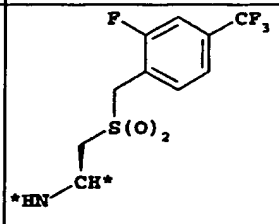
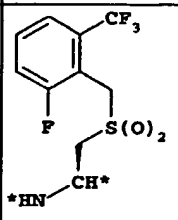
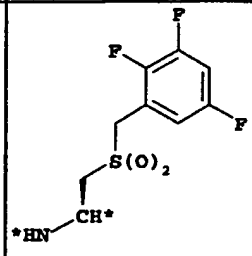
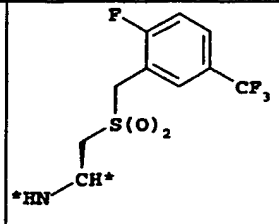
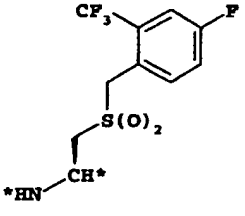
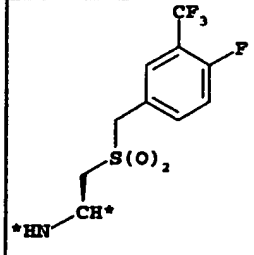
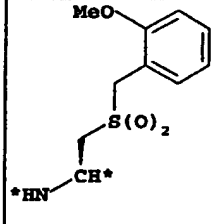
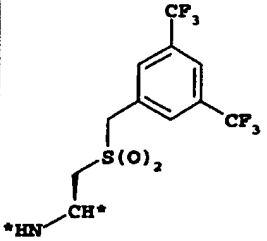
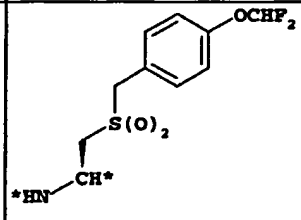
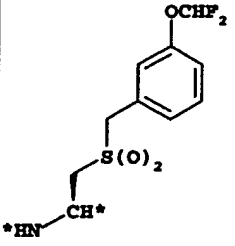
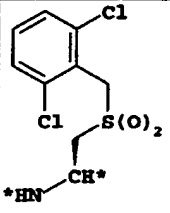
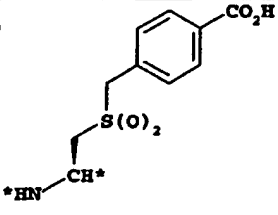
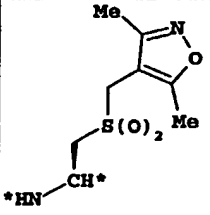
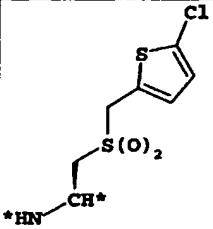
| B52 |  | B53 |  | B54 |  |
| B55 |  | B56 |  | B57 |  |
| B58 |  | B59 |  | B60 |  |
| B61 |  | B62 |  | B63 |  |
| B64 |  | B65 |  | B66 |  |
| B67 |  | B68 |  | B69 |  |

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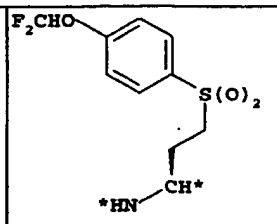
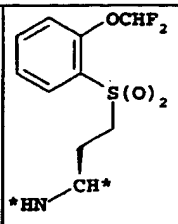
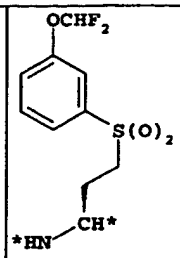
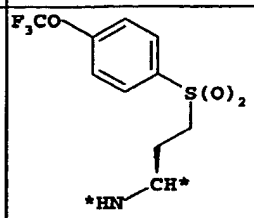
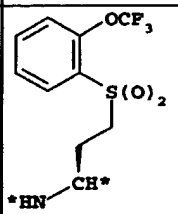
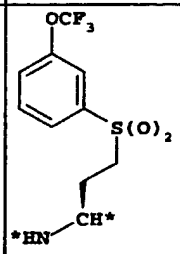
| B70 |  | B71 |  | B72 |  |
| B73 |  | B74 |  | B75 |  |

TABLE 3

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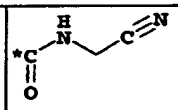
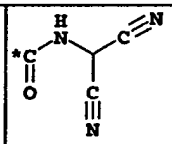
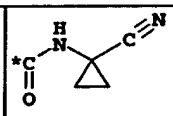
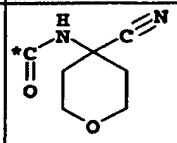
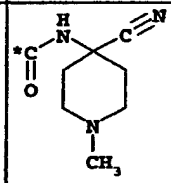
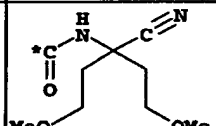
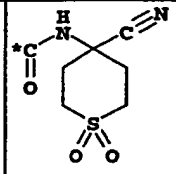
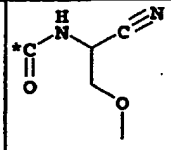
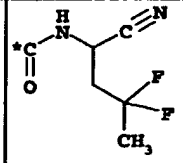
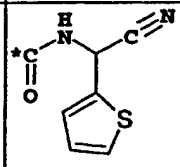
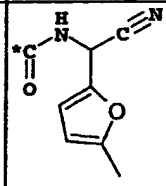
| C1 |  | C2 |  | C3 |  |
| C4 |  | C5 |  | C6 |  |
| C7 |  | C8 |  | C9 |  |
| C10 |  | C11 |  | | |

Particularly preferred examples of fragments "A", "B", and "C" are illustrated below:

| | | | | | |
|---|---|---|---|---|---|
| A1-B1-C1; | A1-B1-C2; | A1-B1-C3; | A1-B1-C4; | A1-B1-C5; | A1-B1-C6; |
| A1-B1-C7; | A1-B1-C8; | A1-B1-C9; | A2-B1-C1; | A2-B1-C2; | A2-B1-C3; |
| A2-B1-C4; | A2-B1-C5; | A2-B1-C6; | A2-B1-C7; | A2-B1-C8; | A2-B1-C9; |
| A3-B1-C1; | A3-B1-C2; | A3-B1-C3; | A3-B1-C4; | A3-B1-C5; | A3-B1-C6; |
| A3-B1-C7; | A3-B1-C8; | A3-B1-C9; | A4-B1-C1; | A4-B1-C2; | A4-B1-C3; |
| A4-B1-C4; | A4-B1-C5; | A4-B1-C6; | A4-B1-C7; | A4-B1-C8; | A4-B1-C9; |
| A5-B1-C1; | A5-B1-C2; | A5-B1-C3; | A5-B1-C4; | A5-B1-C5; | A5-B1-C6; |
| A5-B1-C7; | A5-B1-C8; | A5-B1-C9; | A6-B1-C1; | A6-B1-C2; | A6-B1-C3; |
| A6-B1-C4; | A6-B1-C5; | A6-B1-C6; | A6-B1-C7; | A6-B1-C8; | A6-B1-C9; |
| A7-B1-C1; | A7-B1-C2; | A7-B1-C3; | A7-B1-C4; | A7-B1-C5; | A7-B1-C6; |
| A7-B1-C7; | A7-B1-C8; | A7-B1-C9; | A8-B1-C1; | A8-B1-C2; | A8-B1-C3; |
| A8-B1-C4; | A8-B1-C5; | A8-B1-C6; | A8-B1-C7; | A8-B1-C8; | A8-B1-C9; |
| A9-B1-C1; | A9-B1-C2; | A9-B1-C3; | A9-B1-C4; | A9-B1-C5; | A9-B1-C6; |
| A9-B1-C7; | A9-B1-C8; | A9-B1-C9; | A10-B1-C1; | A10-B1-C2; | A10-B1-C3; |
| A10-B1-C4; | A10-B1-C5; | A10-B1-C6; | A10-B1-C7; | A10-B1-C8; | A10-B1-C9; |
| A11-B1-C1; | A11-B1-C2; | A11-B1-C3; | A11-B1-C4; | A11-B1-C5; | A11-B1-C6; |
| A11-B1-C7; | A11-B1-C8; | A11-B1-C9; | A12-B1-C1; | A12-B1-C2; | A12-B1-C3; |
| A12-B1-C4; | A12-B1-C5; | A12-B1-C6; | A12-B1-C7; | A12-B1-C8; | A12-B1-C9; |
| A13-B1-C1; | A13-B1-C2; | A13-B1-C3; | A13-B1-C4; | A13-B1-C5; | A13-B1-C6; |
| A13-B1-C7; | A13-B1-C8; | A13-B1-C9; | A14-B1-C1; | A14-B1-C2; | A14-B1-C3; |
| A14-B1-C4; | A14-B1-C5; | A14-B1-C6; | A14-B1-C7; | A14-B1-C8; | A14-B1-C9; |
| A15-B1-C1; | A15-B1-C2; | A15-B1-C3; | A15-B1-C4; | A15-B1-C5; | A15-B1-C6; |
| A15-B1-C7; | A15-B1-C8; | A15-B1-C9; | A16-B1-C1; | A16-B1-C2; | A16-B1-C3; |
| A16-B1-C4; | A16-B1-C5; | A16-B1-C6; | A16-B1-C7; | A16-B1-C8; | A16-B1-C9; |
| A17-B1-C1; | A17-B1-C2; | A17-B1-C3; | A17-B1-C4; | A17-B1-C5; | A17-B1-C6; |
| A17-B1-C7; | A17-B1-C8; | A17-B1-C9; | A18-B1-C1; | A18-B1-C2; | A18-B1-C3; |
| A18-B1-C4; | A18-B1-C5; | A18-B1-C6; | A18-B1-C7; | A18-B1-C8; | A18-B1-C9; |
| A19-B1-C1; | A19-B1-C2; | A19-B1-C3; | A19-B1-C4; | A19-B1-C5; | A19-B1-C6; |
| A19-B1-C7; | A19-B1-C8; | A19-B1-C9; | A20-B1-C1; | A20-B1-C2; | A20-B1-C3; |
| A20-B1-C4; | A20-B1-C5; | A20-B1-C6; | A20-B1-C7; | A20-B1-C8; | A20-B1-C9; |
| A21-B1-C1; | A21-B1-C2; | A21-B1-C3; | A21-B1-C4; | A21-B1-C5; | A21-B1-C6; |
| A21-B1-C7; | A21-B1-C8; | A21-B1-C9; | A22-B1-C1; | A22-B1-C2; | A22-B1-C3; |
| A22-B1-C4; | A22-B1-C5; | A22-B1-C6; | A22-B1-C7; | A22-B1-C8; | A22-B1-C9; |
| A23-B1-C1; | A23-B1-C2; | A23-B1-C3; | A23-B1-C4; | A23-B1-C5; | A23-B1-C6; |
| A23-B1-C7; | A23-B1-C8; | A23-B1-C9; | A24-B1-C1; | A24-B1-C2; | A24-B1-C3; |
| A24-B1-C4; | A24-B1-C5; | A24-B1-C6; | A24-B1-C7; | A24-B1-C8; | A24-B1-C9; |
| A25-B1-C1; | A25-B1-C2; | A25-B1-C3; | A25-B1-C4; | A25-B1-C5; | A25-B1-C6; |
| A25-B1-C7; | A25-B1-C8; | A25-B1-C9; | A26-B1-C1; | A26-B1-C2; | A26-B1-C3; |
| A26-B1-C4; | A26-B1-C5; | A26-B1-C6; | A26-B1-C7; | A26-B1-C8; | A26-B1-C9; |
| A27-B1-C1; | A27-B1-C2; | A27-B1-C3; | A27-B1-C4; | A27-B1-C5; | A27-B1-C6; |
| A27-B1-C7; | A27-B1-C8; | A27-B1-C9; | A28-B1-C1; | A28-B1-C2; | A28-B1-C3; |
| A28-B1-C4; | A28-B1-C5; | A28-B1-C6; | A28-B1-C7; | A28-B1-C8; | A28-B1-C9; |
| A29-B1-C1; | A29-B1-C2; | A29-B1-C3; | A29-B1-C4; | A29-B1-C5; | A29-B1-C6; |
| A29-B1-C7; | A29-B1-C8; | A29-B1-C9; | A30-B1-C1; | A30-B1-C2; | A30-B1-C3; |
| A30-B1-C4; | A30-B1-C5; | A30-B1-C6; | A30-B1-C7; | A30-B1-C8; | A30-B1-C9; |
| A31-B1-C1; | A31-B1-C2; | A31-B1-C3; | A31-B1-C4; | A31-B1-C5; | A31-B1-C6; |
| A31-B1-C7; | A31-B1-C8; | A31-B1-C9; | A32-B1-C1; | A32-B1-C2; | A32-B1-C3; |
| A32-B1-C4; | A32-B1-C5; | A32-B1-C6; | A32-B1-C7; | A32-B1-C8; | A32-B1-C9; |
| A33-B1-C1; | A33-B1-C2; | A33-B1-C3; | A33-B1-C4; | A33-B1-C5; | A33-B1-C6; |
| A33-B1-C7; | A33-B1-C8; | A33-B1-C9; | A34-B1-C1; | A34-B1-C2; | A34-B1-C3; |
| A34-B1-C4; | A34-B1-C5; | A34-B1-C6; | A34-B1-C7; | A34-B1-C8; | A34-B1-C9; |
| A35-B1-C1; | A35-B1-C2; | A35-B1-C3; | A35-B1-C4; | A35-B1-C5; | A35-B1-C6; |

A35-B1-C7; A35-B1-C8; A35-B1-C9; A36-B1-C1; A36-B1-C2; A36-B1-C3;
A36-B1-C4; A36-B1-C5; A36-B1-C6; A36-B1-C7; A36-B1-C8; A36-B1-C9;
A37-B1-C1; A37-B1-C2; A37-B1-C3; A37-B1-C4; A37-B1-C5; A37-B1-C6;
A37-B1-C7; A37-B1-C8; A37-B1-C9; A38-B1-C1; A38-B1-C2; A38-B1-C3;
A38-B1-C4; A38-B1-C5; A38-B1-C6; A38-B1-C7; A38-B1-C8; A38-B1-C9;
A39-B1-C1; A39-B1-C2; A39-B1-C3; A39-B1-C4; A39-B1-C5; A39-B1-C6;
A39-B1-C7; A39-B1-C8; A39-B1-C9; A40-B1-C1; A40-B1-C2; A40-B1-C3;
A40-B1-C4; A40-B1-C5; A40-B1-C6; A40-B1-C7; A40-B1-C8; A40-B1-C9;
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A41-B1-C7; A41-B1-C8; A41-B1-C9; A42-B1-C1; A42-B1-C2; A42-B1-C3;
A42-B1-C4; A42-B1-C5; A42-B1-C6; A42-B1-C7; A42-B1-C8; A42-B1-C9;
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A43-B1-C7; A43-B1-C8; A43-B1-C9; A44-B1-C1; A44-B1-C2; A44-B1-C3;
A44-B1-C4; A44-B1-C5; A44-B1-C6; A44-B1-C7; A44-B1-C8; A44-B1-C9;
A45-B1-C1; A45-B1-C2; A45-B1-C3; A45-B1-C4; A45-B1-C5; A45-B1-C6;
A45-B1-C7; A45-B1-C8; A45-B1-C9; A46-B1-C1; A46-B1-C2; A46-B1-C3;
A46-B1-C4; A46-B1-C5; A46-B1-C6; A46-B1-C7; A46-B1-C8; A46-B1-C9;
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A47-B1-C7; A47-B1-C8; A47-B1-C9; A48-B1-C1; A48-B1-C2; A48-B1-C3;
A48-B1-C4; A48-B1-C5; A48-B1-C6; A48-B1-C7; A48-B1-C8; A48-B1-C9;
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A49-B1-C7; A49-B1-C8; A49-B1-C9; A50-B1-C1; A50-B1-C2; A50-B1-C3;
A50-B1-C4; A50-B1-C5; A50-B1-C6; A50-B1-C7; A50-B1-C8; A50-B1-C9;
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A53-B1-C1; A53-B1-C2; A53-B1-C3; A53-B1-C4; A53-B1-C5; A53-B1-C6;
A53-B1-C7; A53-B1-C8; A53-B1-C9; A54-B1-C1; A54-B1-C2; A54-B1-C3;
A54-B1-C4; A54-B1-C5; A54-B1-C6; A54-B1-C7; A54-B1-C8; A54-B1-C9;
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A55-B1-C7; A55-B1-C8; A55-B1-C9; A56-B1-C1; A56-B1-C2; A56-B1-C3;
A56-B1-C4; A56-B1-C5; A56-B1-C6; A56-B1-C7; A56-B1-C8; A56-B1-C9;
A57-B1-C1; A57-B1-C2; A57-B1-C3; A57-B1-C4; A57-B1-C5; A57-B1-C6;
A57-B1-C7; A57-B1-C8; A57-B1-C9; A58-B1-C1; A58-B1-C2; A58-B1-C3;
A58-B1-C4; A58-B1-C5; A58-B1-C6; A58-B1-C7; A58-B1-C8; A58-B1-C9;
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A60-B1-C4; A60-B1-C5; A60-B1-C6; A60-B1-C7; A60-B1-C8; A60-B1-C9;
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A61-B1-C7; A61-B1-C8; A61-B1-C9; A62-B1-C1; A62-B1-C2; A62-B1-C3;
A62-B1-C4; A62-B1-C5; A62-B1-C6; A62-B1-C7; A62-B1-C8; A62-B1-C9;
A63-B1-C1; A63-B1-C2; A63-B1-C3; A63-B1-C4; A63-B1-C5; A63-B1-C6;
A63-B1-C7; A63-B1-C8; A63-B1-C9; A64-B1-C1; A64-B1-C2; A64-B1-C3;
A64-B1-C4; A64-B1-C5; A64-B1-C6; A64-B1-C7; A64-B1-C8; A64-B1-C9;
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A65-B1-C7; A65-B1-C8; A65-B1-C9; A66-B1-C1; A66-B1-C2; A66-B1-C3;
A66-B1-C4; A66-B1-C5; A66-B1-C6; A66-B1-C7; A66-B1-C8; A66-B1-C9;
A67-B1-C1; A67-B1-C2; A67-B1-C3; A67-B1-C4; A67-B1-C5; A67-B1-C6;
A67-B1-C7; A67-B1-C8; A67-B1-C9; A68-B1-C1; A68-B1-C2; A68-B1-C3;
A68-B1-C4; A68-B1-C5; A68-B1-C6; A68-B1-C7; A68-B1-C8; A68-B1-C9;
A69-B1-C1; A69-B1-C2; A69-B1-C3; A69-B1-C4; A69-B1-C5; A69-B1-C6;
A69-B1-C7; A69-B1-C8; A69-B1-C9; A70-B1-C1; A70-B1-C2; A70-B1-C3;
A70-B1-C4; A70-B1-C5; A70-B1-C6; A70-B1-C7; A70-B1-C8; A70-B1-C9;
A71-B1-C1; A71-B1-C2; A71-B1-C3; A71-B1-C4; A71-B1-C5; A71-B1-C6;
A71-B1-C7; A71-B1-C8; A71-B1-C9; A1-B2-C1; A1-B2-C2; A1-B2-C3;

| | | | | | |
|---|---|---|---|---|---|
| A1-B2-C4; | A1-B2-C5; | A1-B2-C6; | A1-B2-C7; | A1-B2-C8; | A1-B2-C9; |
| A2-B2-C1; | A2-B2-C2; | A2-B2-C3; | A2-B2-C4; | A2-B2-C5; | A2-B2-C6; |
| A2-B2-C7; | A2-B2-C8; | A2-B2-C9; | A3-B2-C1; | A3-B2-C2; | A3-B2-C3; |
| A3-B2-C4; | A3-B2-C5; | A3-B2-C6; | A3-B2-C7; | A3-B2-C8; | A3-B2-C9; |
| A4-B2-C1; | A4-B2-C2; | A4-B2-C3; | A4-B2-C4; | A4-B2-C5; | A4-B2-C6; |
| A4-B2-C7; | A4-B2-C8; | A4-B2-C9; | A5-B2-C1; | A5-B2-C2; | A5-B2-C3; |
| A5-B2-C4; | A5-B2-C5; | A5-B2-C6; | A5-B2-C7; | A5-B2-C8; | A5-B2-C9; |
| A6-B2-C1; | A6-B2-C2; | A6-B2-C3; | A6-B2-C4; | A6-B2-C5; | A6-B2-C6; |
| A6-B2-C7; | A6-B2-C8; | A6-B2-C9; | A7-B2-C1; | A7-B2-C2; | A7-B2-C3; |
| A7-B2-C4; | A7-B2-C5; | A7-B2-C6; | A7-B2-C7; | A7-B2-C8; | A7-B2-C9; |
| A8-B2-C1; | A8-B2-C2; | A8-B2-C3; | A8-B2-C4; | A8-B2-C5; | A8-B2-C6; |
| A8-B2-C7; | A8-B2-C8; | A8-B2-C9; | A9-B2-C1; | A9-B2-C2; | A9-B2-C3; |
| A9-B2-C4; | A9-B2-C5; | A9-B2-C6; | A9-B2-C7; | A9-B2-C8; | A9-B2-C9; |
| A10-B2-C1; | A10-B2-C2; | A10-B2-C3; | A10-B2-C4; | A10-B2-C5; | A10-B2-C6; |
| A10-B2-C7; | A10-B2-C8; | A10-B2-C9; | A11-B2-C1; | A11-B2-C2; | A11-B2-C3; |
| A11-B2-C4; | A11-B2-C5; | A11-B2-C6; | A11-B2-C7; | A11-B2-C8; | A11-B2-C9; |
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| A12-B2-C7; | A12-B2-C8; | A12-B2-C9; | A13-B2-C1; | A13-B2-C2; | A13-B2-C3; |
| A13-B2-C4; | A13-B2-C5; | A13-B2-C6; | A13-B2-C7; | A13-B2-C8; | A13-B2-C9; |
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| A14-B2-C7; | A14-B2-C8; | A14-B2-C9; | A15-B2-C1; | A15-B2-C2; | A15-B2-C3; |
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| A16-B2-C7; | A16-B2-C8; | A16-B2-C9; | A17-B2-C1; | A17-B2-C2; | A17-B2-C3; |
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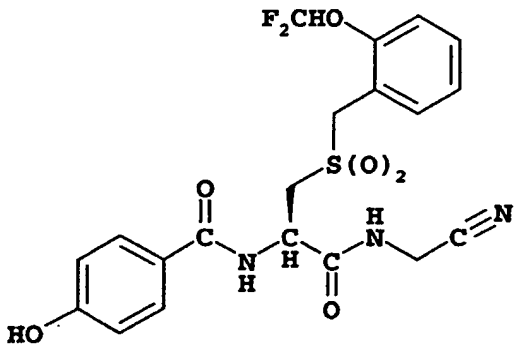
A64-B74-C7; A64-B74-C8; A64-B74-C9; A65-B74-C1; A65-B74-C2; A65-B74-C3;
A65-B74-C4; A65-B74-C5; A65-B74-C6; A65-B74-C7; A65-B74-C8; A65-B74-C9;
A66-B74-C1; A66-B74-C2; A66-B74-C3; A66-B74-C4; A66-B74-C5; A66-B74-C6;
A66-B74-C7; A66-B74-C8; A66-B74-C9; A67-B74-C1; A67-B74-C2; A67-B74-C3;
A67-B74-C4; A67-B74-C5; A67-B74-C6; A67-B74-C7; A67-B74-C8; A67-B74-C9;
A68-B74-C1; A68-B74-C2; A68-B74-C3; A68-B74-C4; A68-B74-C5; A68-B74-C6;
A68-B74-C7; A68-B74-C8; A68-B74-C9; A69-B74-C1; A69-B74-C2; A69-B74-C3;
A69-B74-C4; A69-B74-C5; A69-B74-C6; A69-B74-C7; A69-B74-C8; A69-B74-C9;
A70-B74-C1; A70-B74-C2; A70-B74-C3; A70-B74-C4; A70-B74-C5; A70-B74-C6;
A70-B74-C7; A70-B74-C8; A70-B74-C9; A71-B74-C1; A71-B74-C2; A71-B74-C3;
A71-B74-C4; A71-B74-C5; A71-B74-C6; A71-B74-C7; A71-B74-C8; A71-B74-C9;
A1-B75-C1; A1-B75-C2; A1-B75-C3; A1-B75-C4; A1-B75-C5; A1-B75-C6;
A1-B75-C7; A1-B75-C8; A1-B75-C9; A2-B75-C1; A2-B75-C2; A2-B75-C3;
A2-B75-C4; A2-B75-C5; A2-B75-C6; A2-B75-C7; A2-B75-C8; A2-B75-C9;
A3-B75-C1; A3-B75-C2; A3-B75-C3; A3-B75-C4; A3-B75-C5; A3-B75-C6;
A3-B75-C7; A3-B75-C8; A3-B75-C9; A4-B75-C1; A4-B75-C2; A4-B75-C3;
A4-B75-C4; A4-B75-C5; A4-B75-C6; A4-B75-C7; A4-B75-C8; A4-B75-C9;
A5-B75-C1; A5-B75-C2; A5-B75-C3; A5-B75-C4; A5-B75-C5; A5-B75-C6;
A5-B75-C7; A5-B75-C8; A5-B75-C9; A6-B75-C1; A6-B75-C2; A6-B75-C3;
A6-B75-C4; A6-B75-C5; A6-B75-C6; A6-B75-C7; A6-B75-C8; A6-B75-C9;
A7-B75-C1; A7-B75-C2; A7-B75-C3; A7-B75-C4; A7-B75-C5; A7-B75-C6;
A7-B75-C7; A7-B75-C8; A7-B75-C9; A8-B75-C1; A8-B75-C2; A8-B75-C3;
A8-B75-C4; A8-B75-C5; A8-B75-C6; A8-B75-C7; A8-B75-C8; A8-B75-C9;
A9-B75-C1; A9-B75-C2; A9-B75-C3; A9-B75-C4; A9-B75-C5; A9-B75-C6;
A9-B75-C7; A9-B75-C8; A9-B75-C9; A10-B75-C1; A10-B75-C2; A10-B75-C3;
A10-B75-C4; A10-B75-C5; A10-B75-C6; A10-B75-C7; A10-B75-C8; A10-B75-C9;
A11-B75-C1; A11-B75-C2; A11-B75-C3; A11-B75-C4; A11-B75-C5; A11-B75-C6;
A11-B75-C7; A11-B75-C8; A11-B75-C9; A12-B75-C1; A12-B75-C2; A12-B75-C3;
A12-B75-C4; A12-B75-C5; A12-B75-C6; A12-B75-C7; A12-B75-C8; A12-B75-C9;
A13-B75-C1; A13-B75-C2; A13-B75-C3; A13-B75-C4; A13-B75-C5; A13-B75-C6;
A13-B75-C7; A13-B75-C8; A13-B75-C9; A14-B75-C1; A14-B75-C2; A14-B75-C3;
A14-B75-C4; A14-B75-C5; A14-B75-C6; A14-B75-C7; A14-B75-C8; A14-B75-C9;
A15-B75-C1; A15-B75-C2; A15-B75-C3; A15-B75-C4; A15-B75-C5; A15-B75-C6;
A15-B75-C7; A15-B75-C8; A15-B75-C9; A16-B75-C1; A16-B75-C2; A16-B75-C3;
A16-B75-C4; A16-B75-C5; A16-B75-C6; A16-B75-C7; A16-B75-C8; A16-B75-C9;
A17-B75-C1; A17-B75-C2; A17-B75-C3; A17-B75-C4; A17-B75-C5; A17-B75-C6;
A17-B75-C7; A17-B75-C8; A17-B75-C9; A18-B75-C1; A18-B75-C2; A18-B75-C3;
A18-B75-C4; A18-B75-C5; A18-B75-C6; A18-B75-C7; A18-B75-C8; A18-B75-C9;
A19-B75-C1; A19-B75-C2; A19-B75-C3; A19-B75-C4; A19-B75-C5; A19-B75-C6;
A19-B75-C7; A19-B75-C8; A19-B75-C9; A20-B75-C1; A20-B75-C2; A20-B75-C3;
A20-B75-C4; A20-B75-C5; A20-B75-C6; A20-B75-C7; A20-B75-C8; A20-B75-C9;
A21-B75-C1; A21-B75-C2; A21-B75-C3; A21-B75-C4; A21-B75-C5; A21-B75-C6;
A21-B75-C7; A21-B75-C8; A21-B75-C9; A22-B75-C1; A22-B75-C2; A22-B75-C3;
A22-B75-C4; A22-B75-C5; A22-B75-C6; A22-B75-C7; A22-B75-C8; A22-B75-C9;
A23-B75-C1; A23-B75-C2; A23-B75-C3; A23-B75-C4; A23-B75-C5; A23-B75-C6;
A23-B75-C7; A23-B75-C8; A23-B75-C9; A24-B75-C1; A24-B75-C2; A24-B75-C3;
A24-B75-C4; A24-B75-C5; A24-B75-C6; A24-B75-C7; A24-B75-C8; A24-B75-C9;

A25-B75-C1; A25-B75-C2; A25-B75-C3; A25-B75-C4; A25-B75-C5; A25-B75-C6;
A25-B75-C7; A25-B75-C8; A25-B75-C9; A26-B75-C1; A26-B75-C2; A26-B75-C3;
A26-B75-C4; A26-B75-C5; A26-B75-C6; A26-B75-C7; A26-B75-C8; A26-B75-C9;
A27-B75-C1; A27-B75-C2; A27-B75-C3; A27-B75-C4; A27-B75-C5; A27-B75-C6;
A27-B75-C7; A27-B75-C8; A27-B75-C9; A28-B75-C1; A28-B75-C2; A28-B75-C3;
A28-B75-C4; A28-B75-C5; A28-B75-C6; A28-B75-C7; A28-B75-C8; A28-B75-C9;
A29-B75-C1; A29-B75-C2; A29-B75-C3; A29-B75-C4; A29-B75-C5; A29-B75-C6;
A29-B75-C7; A29-B75-C8; A29-B75-C9; A30-B75-C1; A30-B75-C2; A30-B75-C3;
A30-B75-C4; A30-B75-C5; A30-B75-C6; A30-B75-C7; A30-B75-C8; A30-B75-C9;
A31-B75-C1; A31-B75-C2; A31-B75-C3; A31-B75-C4; A31-B75-C5; A31-B75-C6;
A31-B75-C7; A31-B75-C8; A31-B75-C9; A32-B75-C1; A32-B75-C2; A32-B75-C3;
A32-B75-C4; A32-B75-C5; A32-B75-C6; A32-B75-C7; A32-B75-C8; A32-B75-C9;
A33-B75-C1; A33-B75-C2; A33-B75-C3; A33-B75-C4; A33-B75-C5; A33-B75-C6;
A33-B75-C7; A33-B75-C8; A33-B75-C9; A34-B75-C1; A34-B75-C2; A34-B75-C3;
A34-B75-C4; A34-B75-C5; A34-B75-C6; A34-B75-C7; A34-B75-C8; A34-B75-C9;
A35-B75-C1; A35-B75-C2; A35-B75-C3; A35-B75-C4; A35-B75-C5; A35-B75-C6;
A35-B75-C7; A35-B75-C8; A35-B75-C9; A36-B75-C1; A36-B75-C2; A36-B75-C3;
A36-B75-C4; A36-B75-C5; A36-B75-C6; A36-B75-C7; A36-B75-C8; A36-B75-C9;
A37-B75-C1; A37-B75-C2; A37-B75-C3; A37-B75-C4; A37-B75-C5; A37-B75-C6;
A37-B75-C7; A37-B75-C8; A37-B75-C9; A38-B75-C1; A38-B75-C2; A38-B75-C3;
A38-B75-C4; A38-B75-C5; A38-B75-C6; A38-B75-C7; A38-B75-C8; A38-B75-C9;
A39-B75-C1; A39-B75-C2; A39-B75-C3; A39-B75-C4; A39-B75-C5; A39-B75-C6;
A39-B75-C7; A39-B75-C8; A39-B75-C9; A40-B75-C1; A40-B75-C2; A40-B75-C3;
A40-B75-C4; A40-B75-C5; A40-B75-C6; A40-B75-C7; A40-B75-C8; A40-B75-C9;
A41-B75-C1; A41-B75-C2; A41-B75-C3; A41-B75-C4; A41-B75-C5; A41-B75-C6;
A41-B75-C7; A41-B75-C8; A41-B75-C9; A42-B75-C1; A42-B75-C2; A42-B75-C3;
A42-B75-C4; A42-B75-C5; A42-B75-C6; A42-B75-C7; A42-B75-C8; A42-B75-C9;
A43-B75-C1; A43-B75-C2; A43-B75-C3; A43-B75-C4; A43-B75-C5; A43-B75-C6;
A43-B75-C7; A43-B75-C8; A43-B75-C9; A44-B75-C1; A44-B75-C2; A44-B75-C3;
A44-B75-C4; A44-B75-C5; A44-B75-C6; A44-B75-C7; A44-B75-C8; A44-B75-C9;
A45-B75-C1; A45-B75-C2; A45-B75-C3; A45-B75-C4; A45-B75-C5; A45-B75-C6;
A45-B75-C7; A45-B75-C8; A45-B75-C9; A46-B75-C1; A46-B75-C2; A46-B75-C3;
A46-B75-C4; A46-B75-C5; A46-B75-C6; A46-B75-C7; A46-B75-C8; A46-B75-C9;
A47-B75-C1; A47-B75-C2; A47-B75-C3; A47-B75-C4; A47-B75-C5; A47-B75-C6;
A47-B75-C7; A47-B75-C8; A47-B75-C9; A48-B75-C1; A48-B75-C2; A48-B75-C3;
A48-B75-C4; A48-B75-C5; A48-B75-C6; A48-B75-C7; A48-B75-C8; A48-B75-C9;
A49-B75-C1; A49-B75-C2; A49-B75-C3; A49-B75-C4; A49-B75-C5; A49-B75-C6;
A49-B75-C7; A49-B75-C8; A49-B75-C9; A50-B75-C1; A50-B75-C2; A50-B75-C3;
A50-B75-C4; A50-B75-C5; A50-B75-C6; A50-B75-C7; A50-B75-C8; A50-B75-C9;
A51-B75-C1; A51-B75-C2; A51-B75-C3; A51-B75-C4; A51-B75-C5; A51-B75-C6;
A51-B75-C7; A51-B75-C8; A51-B75-C9; A52-B75-C1; A52-B75-C2; A52-B75-C3;
A52-B75-C4; A52-B75-C5; A52-B75-C6; A52-B75-C7; A52-B75-C8; A52-B75-C9;
A53-B75-C1; A53-B75-C2; A53-B75-C3; A53-B75-C4; A53-B75-C5; A53-B75-C6;
A53-B75-C7; A53-B75-C8; A53-B75-C9; A54-B75-C1; A54-B75-C2; A54-B75-C3;
A54-B75-C4; A54-B75-C5; A54-B75-C6; A54-B75-C7; A54-B75-C8; A54-B75-C9;
A55-B75-C1; A55-B75-C2; A55-B75-C3; A55-B75-C4; A55-B75-C5; A55-B75-C6;
A55-B75-C7; A55-B75-C8; A55-B75-C9; A56-B75-C1; A56-B75-C2; A56-B75-C3;
A56-B75-C4; A56-B75-C5; A56-B75-C6; A56-B75-C7; A56-B75-C8; A56-B75-C9;
A57-B75-C1; A57-B75-C2; A57-B75-C3; A57-B75-C4; A57-B75-C5; A57-B75-C6;
A57-B75-C7; A57-B75-C8; A57-B75-C9; A58-B75-C1; A58-B75-C2; A58-B75-C3;
A58-B75-C4; A58-B75-C5; A58-B75-C6; A58-B75-C7; A58-B75-C8; A58-B75-C9;
A59-B75-C1; A59-B75-C2; A59-B75-C3; A59-B75-C4; A59-B75-C5; A59-B75-C6;
A59-B75-C7; A59-B75-C8; A59-B75-C9; A60-B75-C1; A60-B75-C2; A60-B75-C3;
A60-B75-C4; A60-B75-C5; A60-B75-C6; A60-B75-C7; A60-B75-C8; A60-B75-C9;
A61-B75-C1; A61-B75-C2; A61-B75-C3; A61-B75-C4; A61-B75-C5; A61-B75-C6;

A61-B75-C7; A61-B75-C8; A61-B75-C9; A62-B75-C1; A62-B75-C2; A62-B75-C3;
A62-B75-C4; A62-B75-C5; A62-B75-C6; A62-B75-C7; A62-B75-C8; A62-B75-C9;
A63-B75-C1; A63-B75-C2; A63-B75-C3; A63-B75-C4; A63-B75-C5; A63-B75-C6;
A63-B75-C7; A63-B75-C8; A63-B75-C9; A64-B75-C1; A64-B75-C2; A64-B75-C3;
A64-B75-C4; A64-B75-C5; A64-B75-C6; A64-B75-C7; A64-B75-C8; A64-B75-C9;
A65-B75-C1; A65-B75-C2; A65-B75-C3; A65-B75-C4; A65-B75-C5; A65-B75-C6;
A65-B75-C7; A65-B75-C8; A65-B75-C9; A66-B75-C1; A66-B75-C2; A66-B75-C3;
A66-B75-C4; A66-B75-C5; A66-B75-C6; A66-B75-C7; A66-B75-C8; A66-B75-C9;
A67-B75-C1; A67-B75-C2; A67-B75-C3; A67-B75-C4; A67-B75-C5; A67-B75-C6;
A67-B75-C7; A67-B75-C8; A67-B75-C9; A68-B75-C1; A68-B75-C2; A68-B75-C3;
A68-B75-C4; A68-B75-C5; A68-B75-C6; A68-B75-C7; A68-B75-C8; A68-B75-C9;
A69-B75-C1; A69-B75-C2; A69-B75-C3; A69-B75-C4; A69-B75-C5; A69-B75-C6;
A69-B75-C7; A69-B75-C8; A69-B75-C9; A70-B75-C1; A70-B75-C2; A70-B75-C3;
A70-B75-C4; A70-B75-C5; A70-B75-C6; A70-B75-C7; A70-B75-C8; A70-B75-C9;
A71-B75-C1; A71-B75-C2; A71-B75-C3; A71-B75-C4; A71-B75-C5; A71-B75-C6;
A71-B75-C7; A71-B75-C8; A71-B75-C9;

Thus, for example, in the above list the compound denoted as A20-B2-C1 is the product of the combination of group A20 in Table 1 and B2 in Table 2 and C1 in Table 3, namely *N*-(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-4-hydroxy-benzamide:




Further preferred are compounds of Formula I selected from a group consisting of:

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide (compound denoted as A24-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-isonicotinamide (compound denoted as A25-B2-C1);

Pyridine-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (compound denoted as A62-B2-C1);

Pyrazine-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (compound denoted as A63-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-6-hydroxy-nicotinamide (compound denoted as A65-B2-C1);

2-Amino-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide, (compound denoted as A67-B2-C1);

6-Amino-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide, (compound denoted as A66-B2-C1);

3-Hydroxy-pyridine-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-

(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (compound denoted as A68-B2-C1);

Morpholine-4-carboxylic acid-{(R)-1-(4-cyano-tetrahydro-pyran-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (compound denoted as A2-B2--C4);

Morpholine-4-carboxylic acid-{(R)-1-(4-cyano-1-methyl-piperidin-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (compound denoted as A2-B2-C5);

(R)-*N* -Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(3, 3-dimethyl-ureido)-propionamide, (compound denoted as A56-B2-C1);

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid allyl ester, (compound denoted as A53-B2-C1);

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid isopropyl ester, (compound denoted as A54-B2-C1);

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid isobutyl ester, (compound denoted as A51-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3,4-difluoro-benzamide, (compound denoted as A46-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-methyl-benzamide, (compound denoted as A48-B2-C1);

Thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A28-B2-C1);

4-Bromo-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-benzamide, (compound denoted as A43-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-4-methoxy-benzamide, (compound denoted as A44-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-

phenylmethanesulfonyl]-ethyl}-4-trifluoromethoxy-benzamide, (compound denoted as A45-B2-C1);

Naphthalene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A7-B2-C1);

(E)-*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-phenyl-acrylamide, (compound denoted as A59-B2-C1);

5-Methyl-thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A31-B2-C1);

Biphenyl-4-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A11-B2-C1);

1H-Indole-5-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A60-B2-C1);

Benzo[1,3]dioxole-5-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A8-B2-C1);

Benzo[b]thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A35-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-phenoxy-benzamide, (compound denoted as A69-B2-C1);

Quinoline-3-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A13-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-(1-phenyl-methanoyl)-benzamide, (compound

denoted as A70-B2-C1);

4-Chloro-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-benzamide, (compound denoted as A42-B2-C1);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-fluoro-4-methoxy-benzamide, (compound denoted as A41-B2-C1);

3-Bromo-thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A33-B2-C1);

3-Chloro-benzo[b]thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A36-B2-C1);

3-Chloro-thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A32-B2-C1);

*N*-{(R)-(Cyanomethyl-carbamoyl)-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-trifluoromethyl-benzamide, (compound denoted as A40-B2-C1);

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(naphthalene-2-sulfonylamino)-propionamide, (compound denoted as A38-B2-C1);

Cyclopentanecarboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide, (compound denoted as A34-B2-C1);

*N*-[1R-cyanomethylcarbamoyl-2-(3-trifluoromethoxybenzylsulfonyl)ethyl]benzamide, (compound denoted as A1-B24-C1);

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]benzamide, (compound denoted as A1-B2-C1);

*N*-[1R-cyanomethylcarbamoyl-2-(2-trifluoromethoxybenzylsulfonyl)ethyl]benzamide, (compound denoted as A1-B42-C1);

*N*-(1R-cyanomethylcarbamoyl-2-(3-difluoromethoxybenzylsulfonyl)ethyl]benzamide, (compound denoted as A1-B24-C1);

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]morpholine-4-carboxamide, (compound denoted as A2-B2-C1);

*N*-[1R-(1-cyanocyclopropylcarbamoyl)-2-(2-difluoromethoxybenzylsulfonyl)ethyl]-morpholine-4-carboxamide, (compound denoted as A2-B2-C3); and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates (e.g. hydrates) of such compounds and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

Particularly preferred compounds are:

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)-ethyl]benzamide;

*N*-[1R-cyanomethylcarbamoyl-2-(2-trifluoromethoxybenzylsulfonyl)-ethyl]benzamide;

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)-ethyl]morpholine-4-carboxamide;

*N*-[1R-(1-cyanocyclopropylcarbamoyl)-2-(2-difluoromethoxybenzylsulfonyl)-ethyl]morpholine-4-carboxamide; and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates (e.g. hydrates) of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

Pharmacology and Utility:

The compounds of the invention are selective inhibitors of cathepsin S and, as such, are useful for treating diseases in which cathepsin S activity contributes to the pathology and/or symptomatology of the disease. For example, the compounds of the invention are useful in treating autoimmune disorders, including, but not limited to, juvenile onset diabetes, multiple sclerosis, pemphigus vulgaris, Graves' disease,

myasthenia gravis, systemic lupus erythemotasus, rheumatoid arthritis and Hashimoto's thyroiditis, allergic disorders, including, but not limited to, asthma, and allogeneic immune responses, including, but not limited to, organ transplants or tissue grafts.

Cathepsin S also is implicated in disorders involving excessive elastolysis, such as chronic obstructive pulmonary disease (e.g., emphysema), bronchiolitis, excessive airway elastolysis in asthma and bronchitis, pneumonities and cardiovascular disease such as plaque rupture and atheroma. Cathepsin S is implicated in fibril formation and, therefore, inhibitors of cathepsins S are of use in treatment of systemic amyloidosis.

The cysteine protease inhibitory activities of the compounds of the invention can be determined by methods known to those of ordinary skill in the art. Suitable *in vitro* assays for measuring protease activity and the inhibition thereof by test compounds are known. Typically, the assay measures protease induced hydrolysis of a peptide based substrate. Details of assays for measuring protease inhibitory activity are set forth in Examples 11, 12, 13 and 14, *infra*.

Administration and Pharmaceutical Compositions:

In general, compounds of Formula I will be administered in therapeutically effective amounts via any of the usual and acceptable modes known in the art, either singly or in combination with another therapeutic agent. A therapeutically effective amount may vary widely depending on the severity of the disease, the age and relative health of the subject, the potency of the compound used and other factors. For example, therapeutically effective amounts of a compound of Formula I may range from about 1 micrograms per kilogram body weight (μg/kg) per day to about 1 milligram per kilogram body weight (mg/kg) per day, typically from about 10 μg/kg/day to about 0.1 mg/kg/day. Therefore, a therapeutically effective amount for a 80 kg human patient may range from about 100 μg/day to about 100 mg/day, typically from about 1 μg/day to about 10 mg/day. In general, one of ordinary skill in the art, acting in reliance upon personal knowledge and the disclosure of this Application, will be able to ascertain a therapeutically effective amount of a compound of Formula I for treating a given disease.

The compounds of Formula I can be administered as pharmaceutical compositions by one of the following routes: oral, systemic (e.g., transdermal, intranasal or by suppository) or parenteral (e.g., intramuscular, intravenous or subcutaneous). Compositions can take the form of tablets, pills, capsules, semisolids, powders, sustained release formulations, solutions, suspensions, elixirs, aerosols, or any other appropriate composition and are comprised of, in general, a compound of Formula I in combination with at least one pharmaceutically acceptable excipient. Acceptable excipients are non-toxic, aid administration, and do not adversely affect the therapeutic benefit of the active ingredient. Such excipient may be any solid, liquid, semisolid or, in the case of an aerosol composition, gaseous excipient that is generally available to one of skill in the art.

Solid pharmaceutical excipients include starch, cellulose, talc, glucose, lactose, sucrose, gelatin, malt, rice, flour, chalk, silica gel, magnesium stearate, sodium stearate, glycerol monostearate, sodium chloride, dried skim milk, and the like. Liquid and semisolid excipients may be selected from water, ethanol, glycerol, propylene glycol and various oils, including those of petroleum, animal, vegetable or synthetic origin (e.g., peanut oil, soybean oil, mineral oil, sesame oil, and the like). Preferred liquid carriers, particularly for injectable solutions, include water, saline, aqueous dextrose and glycols.

The amount of a compound of Formula I in the composition may vary widely depending upon the type of formulation, size of a unit dosage, kind of excipients and other factors known to those of skill in the art of pharmaceutical sciences. In general, a composition of a compound of Formula I for treating a given disease will comprise from 0.01%w to 10%w, preferably 0.3%w to 1%w, of active ingredient with the remainder being the excipient or excipients. Preferably the pharmaceutical composition is administered in a single unit dosage form for continuous treatment or in a single unit dosage form ad libitum when relief of symptoms is specifically required. Representative pharmaceutical formulations containing a compound of Formula I are described in Example 15.

Chemistry:

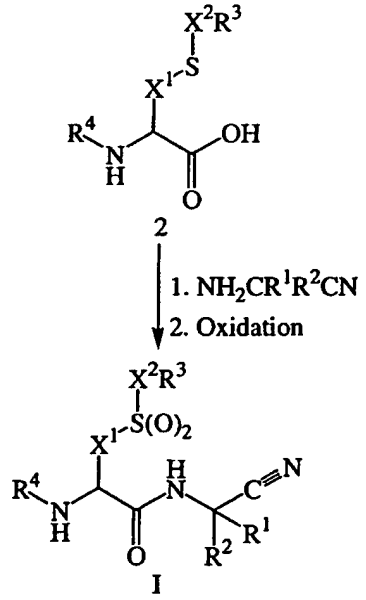
Compounds of the invention may be prepared by the application or adaptation of known methods, by which is meant methods used heretofore or described in the literature, for example those described by R.C. Larock in Comprehensive Organic Transformations, VCH publishers, 1989.

In reactions described hereinafter it may be necessary to protect reactive functional groups, for example hydroxy, amino, imino, thio or carboxy groups, where these are desired in the final product, to avoid their unwanted participation in the reactions. Conventional protecting groups may be used in accordance with standard practice, for examples see T.W. Greene and P.G.M. Wuts in "Protective Groups in Organic Chemistry", John Wiley and Sons, 1999.

Processes for Making Compounds of Formula I:

Compounds of Formula I can be prepared by proceeding as in the following Reaction Scheme 1:

Reaction Scheme 1




in which each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined for Formula I in the Summary of the Invention.

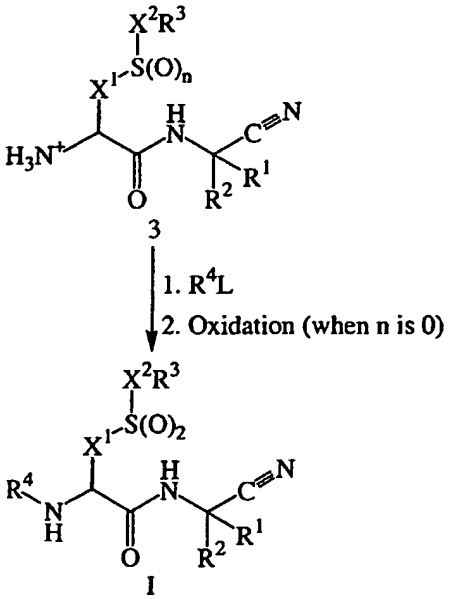
Compounds of Formula I can be prepared by condensing an acid of Formula 2 with an aminoalkanonitrile of the formula $NH_2CR^1R^2CN$ and then oxidizing. The

condensation reaction can be effected with an appropriate coupling agent (e.g., benzotriazol-1-yloxytrispyrrolidinophosphonium hexafluorophosphate (PyBOP®), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), *O*-benzotriazol-1-yl-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate (HBTU), 1,3-dicyclohexylcarbodiimide (DCC), or the like) and optionally an appropriate catalyst (e.g., 1-hydroxybenzotriazole (HOBt), 1-hydroxy-7-azabenzotriazole (HOAt), *O*-(7-azabenzotrizol-1-yl)-1,1,3,3, tetra-methyluroniumhexafluorophosphate (HATU), or the like) and non-nucleophilic base (e.g., *N*-methylpyrrolidinone, *N*-methylmorpholine, and the like, or any suitable combination thereof) at ambient temperature and requires 5 to 10 hours to complete.

The oxidation can be carried out with an oxidizing agent (e.g., Oxone®, or the like) in a suitable solvent (e.g., methanol, water, or the like, or any suitable combination thereof) at ambient temperature and requires 16 to 24 hours to complete. A detailed description for the synthesis of a compound of Formula I by the processes in Reaction Scheme 1 is set forth in the Examples 1, 2, 8 and 10, infra.

Compounds of Formula I can be prepared by proceeding as in the following Reaction Scheme 2:

Reaction Scheme 2



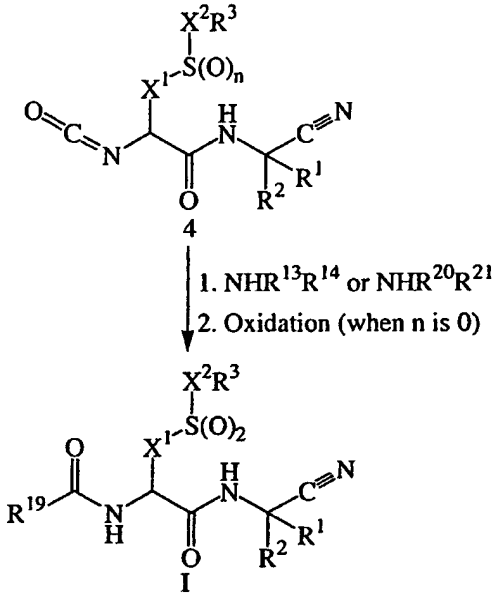
in which n is 0 or 2, L is a leaving group and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined for Formula I in the Summary of the Invention.

Compounds of Formula I can be prepared by condensing a compound of Formula 3 with a compound of the formula $R^4L$ (e.g., 3-acetylbenzoic acid, nicotinic acid, morpholin-4-ylcarbonyl chloride, or the like) and then oxidizing when n is 0. When L is chloro the condensation can be carried out at ambient temperature in the presence of a suitable non-nucleophilic base (e.g., triethylamine, *N*-methylmorpholine, or the like) in a suitable solvent (e.g., dichloromethane, tetrahydrofuran, or the like) and requires 16 to 24 hours to complete. When L is hydroxy the condensation typically is effected in the presence of a suitable coupling agent (e.g., (PyBOP®), EDCI, HBTU, DCC, or the like) and optionally an appropriate catalyst (e.g., 1-hydroxybenzotriazole (HOBt), 1-hydroxy-7-azabenzotriazole (HOAt), or the like) in a suitable solvent (e.g., dichloromethane, tetrahydrofuran, or the like, or any suitable combination thereof) at ambient temperature and requires 16 to 24 hours to complete.

The oxidization can be carried out by the process described above for Reaction Scheme 1. Detailed procedures for the syntheses of compounds of Formula I by the processes described in Scheme 2 are set forth in the Examples 3, 4 and 5, infra.

Compounds of Formula I in which $R^4$ is $-NR^{13}R^{14}$ or $-NR^{20}R^{21}$ can be prepared by proceeding as in the following Reaction Scheme 3:

Reaction Scheme 3

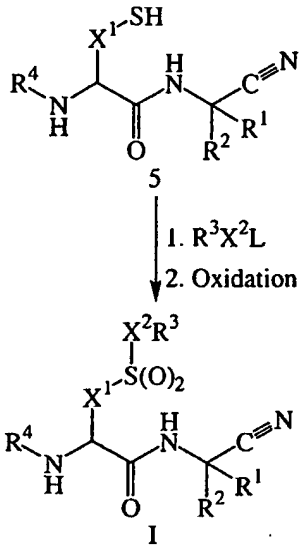



in which $R^{19}$ is $-NR^{13}R^{14}$ or $-NR^{20}R^{21}$, wherein $R^{20}$ and $R^{21}$ together with the nitrogen atom to which $R^{20}$ and $R^{21}$ are attached form hetero($C_{5-12}$)cycloalkyl and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$, $R^{13}$ and $R^{14}$ are as defined in the Summary of the Invention.

Compounds of Formula I in which $R^4$ is $-C(O)NR^{13}R^{14}$ or $-C(O)NR^{20}R^{21}$, wherein $R^{20}$ and $R^{21}$ together with the nitrogen atom to which $R^{20}$ and $R^{21}$ are attached form hetero($C_{5-12}$)cycloalkyl and $R^{13}$ and $R^{14}$ are as defined in the Summary of the Invention can be prepared by condensing a compound of Formula 4 with a compound of the formula $NHR^{13}R^{14}$ or $NHR^{20}R^{21}$, respectively, and then oxidizing when n is 0. The condensation reaction can be carried out at ambient temperature in a suitable solvent (e.g., dichloromethane, or the like) and requires 16 to 24 hours to complete. The oxidization can be carried out by the process described above for Reaction Scheme 1. A detailed description for the synthesis of a compound of Formula I by the processes in Scheme 3 is set forth in the Example 6, infra.

Compounds of Formula I can be prepared by proceeding as in the following Reaction Scheme 4:

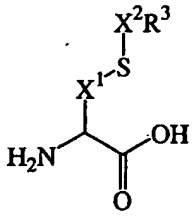
Reaction Scheme 4




in which L is a leaving group and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined for Formula I in the Summary of the Invention.

Compounds of Formula I can be prepared by reacting a compound of Formula 5 with a compound of the formula $R^3X^2L$ and then oxidizing. The reaction is carried out in the presence of base (e.g., potassium hydroxide, or the like) at ambient temperature and requires 2 to 3 hours to complete. The oxidization can be carried out by the process described above for Reaction Scheme 1. A detailed description for the synthesis of a compound of Formula I by the processes in Scheme 4 is set forth in the Examples 7 and 9, infra.

Compounds of Formula 2 can be prepared by reacting a compound of Formula 6:

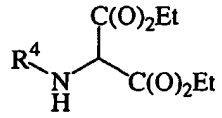



6

with a compound of the formula $R^4L$, in which L is a leaving group and $X^1$, $X^2$ and $R^3$ are as defined in the Summary of the Invention. The reaction can be carried out in the

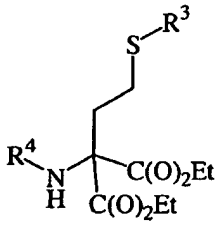
presence of base (e.g., 1 N aqueous sodium hydroxide, or the like) at about 5° C. A detailed description for the synthesis of a compound of Formula 2 by the processes described above is set forth in the References 1 and 7, infra. Compounds of Formula 6 are commercially available or otherwise can be prepared by methods known in the art or analogous to those described elsewhere in this Application.

Compounds of Formula 2 in which $X^1$ is ethylene can be prepared by condensing a diester of Formula 7:



7

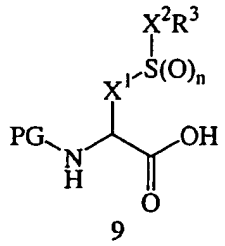
with a compound of the formula $R^3SCH_2CH_2L$ to provide a compound of Formula 8:



8

in which L is a leaving group and $R^3$ and $R^4$ are as defined in the Summary of the Invention, decarbalkoxylating to provide a corresponding monoester and then converting the monoester to a corresponding carboxylic acid. The condensation reaction can be carried out in the presence of a suitable non-nucleophilic base (e.g., *N*-methylpyrrolidone) and lithium hydroxide. The decarbalkoxylation can be effected under strongly basic conditions (e.g., in the presence of 1 N aqueous sodium hydroxide) in a suitable solvent (e.g, methanol) and requires 4 to 6 hours to complete. A detailed description for the synthesis of a compound of Formula 2 by the processes described above is set forth in the Reference 2, infra.

Compounds of Formula 3 can be prepared by condensing a compound of Formula 9:

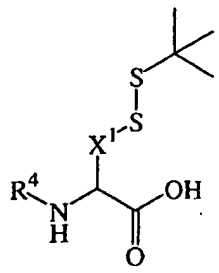


9

with an aminoalkanonitrile of the formula $NH_2CR^1R^2CN$, in which PG is a protecting group and each $X^1$, $R^1$, $R^2$ and $R^3$ are as defined in the Summary of the Invention, optionally oxidizing and then deprotecting. The condensation reaction can be effected with an appropriate condensing agent (e.g., *N*,*N*-dicyclohexyldiimide, diisopropylcarbodiimide, carbonyldiimidazole, or the like) and a suitable non-nucleophilic base (e.g., *N*-methylpyrrolidinone, *N*-methylmorpholine, or the like, or any suitable combination thereof) in a suitable solvent (e.g., dichloromethane, or the like) at ambient temperature and requires 2 to 3 days to complete. Oxidization can be carried out by the process described above for Reaction Scheme 1. Deprotection can be effected by any means which removes the protective group and gives the desired product in reasonable yield. A detailed description of the techniques applicable to the creation of protective groups and their removal can be found in T.W. Greene, *Protective Groups in Organic Synthesis*, 3rd edition, John Wiley & Sons, Inc. 1999. A convenient method of deprotecting is by treatment with a suitable acid (e.g., *p*-toluenesulfonic acid, or the like) providing the acid addition salt in the process. A detailed description for the synthesis of a compound of Formula 3 by the processes described above is set forth in the References 3, 4 and 5, infra.

Compounds of Formula 4 can be prepared by reacting a compound of Formula 3 with phosgene. The reaction is carried out conveniently in a biphasic solvent (e.g., an equal mixture of dichloromethane and saturated sodium bicarbonate solution at ambient temperature. A detailed description for the synthesis of a compound of Formula 4 by the processes described above is set forth in the Reference 6, infra.

Compounds of Formula 5 can be prepared by sequentially condensing an acid of Formula 10:



10

with an aminoalkanonitrile of the formula $NHR^2CR^3R^4CN$ and a compound of the formula $R^4L$ and then deprotecting. The condensation reaction is carried out in a fashion analogous to the process described above for the preparation of the compounds of Formula 3. The condensation reaction with the compound of the formula $R^4L$ is carried out in a fashion analogous to the process described above for the preparation of the compounds of Formula I by Scheme 2. The deprotection can be effected by treatment with a suitable reducing agent (e.g., tris-butyl phosphine, tris-carboxyethyl phosphine, or the like) in the presence of base (e.g., aqueous potassium hydroxide, or the like) in a suitable solvent (e.g., DMF, or the like) under an inert atmosphere and at ambient temperature and requires 12 to 24 hours. A detailed description for the synthesis of a compound of Formula 5 by the processes decribed above is set forth in the Reference 8, infra.

Additional Processes for Preparing Compounds of Formula I:

A compound of Formula I can be prepared as a pharmaceutically acceptable acid addition salt by reacting the free base form of the compound with a pharmaceutically acceptable inorganic or organic acid. Alternatively, a pharmaceutically acceptable base addition salt of a compound of Formula I can be prepared by reacting the free acid form of the compound with a pharmaceutically acceptable inorganic or organic base. Inorganic and organic acids and bases suitable for the preparation of the pharmaceutically acceptable salts of compounds of Formula I are set forth in the definitions section of this Application. Alternatively, the salt forms of the compounds of Formula I can be prepared using salts of the starting materials or intermediates.

The free acid or free base forms of the compounds of Formula I can be prepared from the corresponding base addition salt or acid addition salt form. For example, a compound of Formula I in an acid addition salt form can be converted to the corresponding free base by treating with a suitable base (e.g., ammonium hydroxide solution, sodium hydroxide, and the like). A compound of Formula I in a base addition salt form can be converted to the corresponding free acid by treating with a suitable acid (e.g., hydrochloric acid, etc).

The *N*-oxides of compounds of Formula I can be prepared by methods known to those of ordinary skill in the art. For example, *N*-oxides can be prepared by treating an unoxidized form of the compound of Formula I with an oxidizing agent (e.g., trifluoroperacetic acid, permaleic acid, perbenzoic acid, peracetic acid, *meta*-chloroperoxybenzoic acid, or the like) in a suitable inert organic solvent (e.g., a halogenated hydrocarbon such as dichloromethane) at approximately 0°C. Alternatively, the *N*-oxides of the compounds of Formula I can be prepared from the *N*-oxide of an appropriate starting material.

Compounds of Formula I in unoxidized form can be prepared from *N*-oxides of compounds of Formula I by treating with a reducing agent (e.g., sulfur, sulfur dioxide, triphenyl phosphine, lithium borohydride, sodium borohydride, phosphorus trichloride, tribromide, or the like) in an suitable inert organic solvent (e.g., acetonitrile, ethanol, aqueous dioxane, or the like) at 0 to 80°C.

Prodrug derivatives of the compounds of Formula I can be prepared by methods known to those of ordinary skill in the art (e.g., for further details see Saulnier *et al.*(1994), *Bioorganic and Medicinal Chemistry Letters*, Vol. 4, p. 1985). For example, appropriate prodrugs can be prepared by reacting a non-derivatized compound of Formula I with a suitable carbamylating agent (e.g., 1,1-acyloxyalkylcarbonochloridate, *para*-nitrophenyl carbonate, or the like).

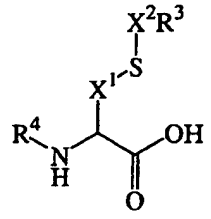
Protected derivatives of the compounds of Formula I can be made by means known to those of ordinary skill in the art. A detailed description of the techniques applicable to the creation of protecting groups and their removal can be found in T.W. Greene, *Protecting Groups in Organic Synthesis*, 3rd edition, John Wiley & Sons, Inc. 1999.

Compounds of the present invention may be conveniently prepared, or formed during the process of the invention, as solvates (e.g. hydrates). Hydrates of compounds of the present invention may be conveniently prepared by recrystallisation from an aqueous/organic solvent mixture, using organic solvents such as dioxan, tetrahydrofuran or methanol.

Compounds of Formula I can be prepared as their individual stereoisomers by reacting a racemic mixture of the compound with an optically active resolving agent to form a pair of diastereoisomeric compounds, separating the diastereomers and recovering the optically pure enantiomer. While resolution of enantiomers can be carried out using covalent diasteromeric derivatives of compounds of Formula I, dissociable complexes are preferred (e.g., crystalline diastereoisomeric salts). Diastereomers have distinct physical properties (e.g., melting points, boiling points, solubilities, reactivity, etc.) and can be readily separated by taking advantage of these dissimilarities. The diastereomers can be separated by chromatography or, preferably, by separation/resolution techniques based upon differences in solubility. The optically pure enantiomer is then recovered, along with the resolving agent, by any practical means that would not result in racemization. A more detailed description of the techniques applicable to the resolution of stereoisomers of compounds from their racemic mixture can be found in Jean Jacques Andre Collet, Samuel H. Wilen, Enantiomers, Racemates and Resolutions, John Wiley & Sons, Inc. (1981).

In summary, the compounds of Formula I are made by a process which comprises:

(A) reacting a compound of Formula 2:

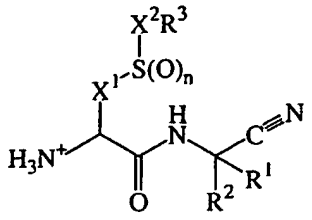


2

with a compound of the formula $NH_2CR^1R^2CN$, in which $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are

as defined in the Summary of the Invention for Formula I; or

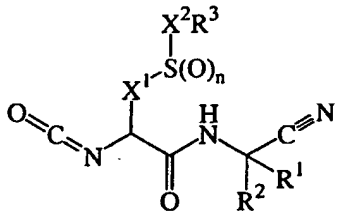
(B) reacting a compound of Formula 3:



3

with a compound of the formula $R^4L$, in which n is 0 or 2, L is a leaving group and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in the Summary of the Invention for Formula I, and then oxidizing when n is 0; or

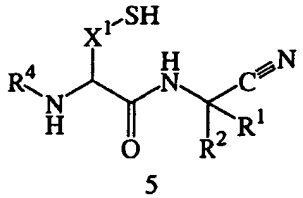
(C) reacting a compound of Formula 4:



4

with a compound of formula $NHR^{13}R^{14}$ or $NHR^{20}R^{21}$ to provide a compound of Formula I in which $R^4$ is $-C(O)NR^{13}R^{14}$ or $-C(O)NR^{20}R^{21}$, respectively, wherein n is 0 or 2, $R^{20}$ and $R^{21}$ together with the nitrogen atom to which $R^{20}$ and $R^{21}$ are attached form hetero($C_{5-12}$)cycloalkyl and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$, $R^{13}$ and $R^{14}$ are as defined in the Summary of the Invention for Formula I, and then oxidizing when n is 0; or

(D) reacting a compound of Formula 5:



5

with a compound of $R^3X^2L$ in which L is a leaving group and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in the Summary of the Invention for Formula I; and

(E) optionally converting a compound of Formula I into a pharmaceutically acceptable salt;

(F) optionally converting a salt form of a compound of Formula I to non-salt form;

(G) optionally converting an unoxidized form of a compound of Formula I into a pharmaceutically acceptable *N*-oxide;

(H) optionally converting an *N*-oxide form of a compound of Formula I its unoxidized form;

(I) optionally resolving an individual isomer of a compound of Formula I from a mixture of isomers;

(J) optionally converting a non-derivatized compound of Formula I into a pharmaceutically prodrug derivative; and

(K) optionally converting a prodrug derivative of a compound of Formula I to its non-derivatized form.

Examples:

The present invention is further exemplified, but not limited by, the following examples that illustrate the preparation of compounds of Formula I (Examples) and intermediates (References) according to the invention.

REFERENCE 1

2*R*-Benzoylamino-3-(4-methylbenzylsulfanyl)propionic acid,

a compound of Formula 2 in which $X^2$ is methylene, $R^3$ is 4-methylphenyl and $R^4$ is benzoyl

A solution comprised of 2*R*-amino-3-(4-methylbenzylsulfanyl)propionic acid (2.25 g, 10 mmol) in 1 N aqueous sodium hydroxide (10 mL) was cooled to -5° C and then treated with benzoyl chloride (1.16 mL, 10 mmol) and 1 N aqueous sodium hydroxide. The reaction was allowed to proceed for 30 minutes and then the mixture was acidified with 1 N aqueous hydrochloric acid (10 mL) to form a precipitate. The precipitate was isolated by filtration to provide 2*R*-benzoylamino-preciptate was

isolated by filtration to provide 2R-benzoylamino-3-(4-methylbenzylsulfanyl)propionic acid (3.38 g, 10 mmol).

REFERENCE 2

2-Benzoylamino-4-phenylsulfanylbutyric acid,

a compound of Formula 2 in which $X^2$ is a bond, $R^3$ is phenyl and $R^4$ is benzoyl

A solution comprised of sodium iodide (7.9 g, 52.7 mmol) and 2-chloroethyl phenyl sulfide (4.7 g, 27.2 mmol) in acetone (40 mL) was refluxed for 15 hours. The reaction mixture was cooled, diluted with ice water and extracted with ethyl acetate. The extract was concentrated and the residue was combined with *N*-methylpyrrolidone (20 mL), lithium hydroxide (1.6 g, 67 mmol) and diethyl 2-benzoylaminomalonate (5 g, 18 mmol). The mixture was stirred at ambient temperature of 15 hours and then poured into cold water. The product was extracted with ethyl acetate and purified by silica gel chromatography to provide diethyl 2-benzoylamino-2-(2-phenylsulfanylethyl)malonate (1.316 g, 3.2 mmol).

The 2-benzoylamino-2-(2-phenylsulfanylethyl)malonate (1.316 g, 3.2 mmol) was dissolved in methanol (10 mL) and the solution was treated with 1 N aqueous sodium hydroxide (7.0 mL) and then stirred at ambient temperature for 4 hours. The mixture was diluted with water and washed with ether (2x). The aqueous layer was cooled on ice, acidified to pH 2 and extracted with ethyl acetate. The extract was dried ($MgSO_4$) and then concentrated. The residue was dissolved in dioxane (30 mL) and the solution was heated at 100° C for 1 hour and then concentrated. Product was purified from the residue by chromatography on silica gel to provide ethyl 2-benzoylamino-4-phenylsulfanylbutyrate (371 mg, 1.1 mmol).

A solution comprised of ethyl 2-benzoylamino-4-phenylsulfanylbutyrate (340 mg, 1.0 mmol) in methanol (4 mL) was treated with 1 N aqueous sodium hydroxide (2 mL) and stirred at ambient temperature for 3 hours. The reaction mixture was cooled on ice, acidified to pH 1 and then extracted with ethyl acetate. The extract was concentrated to provide 2-benzoylamino-4-phenylsulfanylbutyric acid (304 mg, 1.0 mmol).

REFERENCE 3

*tert*-Butyl 2-benzylsulfanyl-1*R*-cyanomethylcarbamoylethylcarbamate

A solution comprised of 3-benzylsulfanyl-2*R*-*tert*-butoxycarbonylaminopropionic acid (50 g, 160.6 mmol) and aminoacetonitrile bisulfate (27.2 g, 176.6 mmol) in dichloromethane (400 mL) was cooled in an ice bath and then treated sequentially with carbonyldiimidazole (31.2 g, 192.7 mmol), dichloromethane (250 mL), and *N*-methylmorpholine (35.3 mL, 321.2 mmol). The mixture was stirred for 5 minutes at 0°C and 2 days at ambient temperature, filtered, concentrated and partitioned between ethyl acetate and water. The ethyl acetate layer was washed with water, saturated potassium phosphate solution, water, saturated sodium bicarbonate solution and brine, dried ($MgSO_4$), filtered and concentrated. The residue was dried under high vacuum to provide *tert*-butyl 2-benzylsulfanyl-1*R*-cyanomethylcarbamoyl-ethylcarbamate (44.1 g, 126.2 mmol) as a white solid.

REFERENCE 4

2*R*-Amino-3-benzylsulfanyl-*N*-cyanomethylpropionamide *para*-toluenesulfonate salt, a compound of Formula 3 in which n is 0, $X^2$ is methylene, $R^1$ and $R^2$ are both hydrogen and $R^3$ is phenyl

Toluenesulfonic acid monhydrate (46.7 g, 246 mmol) was dissolved in 2-propanol (200 mL) and the solution was treated with toluene (600 mL). The solvents were removed under reduced pressure and the residue was dissolved in toluene (400 mL). The solution was concentrated under reduced pressure and the residue was dried under high vacuum. The residue was dissolved in anhydrous diethyl ether (200 mL) and the solution was added to a suspension comprised of *tert*-butyl 2-benzylsulfanyl-1*R*-cyanomethylcarbamoyl-ethyl-carbamate (42 g, 120 mmol), prepared as in Reference 3, in anhydrous diethyl ether (700 mL). The mixture was stirred at ambient temperature for approximately 12 hours and then the supernatant was decanted. The residue was dissolved in a small amount of dichloromethane and product was precipitated out with diethyl ether to provide 2*R*-amino-3-benzylsulfanyl-

*N*-cyanomethylpropionamide *para*-toluenesulfonate salt (50.7 g, 102 mmol).

REFERENCE 5

2*R*-Amino-3-benzylsulfonyl-*N*-cyanomethylpropionamide methanesulfonate salt, a compound of Formula 3 in which n is 2, $X^2$ is a methylene, $R^1$ and $R^2$ are both hydrogen and $R^3$ is phenyl

A solution comprised of *tert*-butyl 2-benzylsulfanyl-1*R*-cyanomethylcarbamoyl-ethylcarbamate (0.2 g, 0.57 mmol), prepared as in Reference 3, in methanol (8 mL) was treated with of Oxone® (0.526 g, 0.86 mmol) in water (8 mL) and the mixture was stirred at 25° C for 2 hours. The mixture then was diluted with cold water and the product was extracted with ethyl acetate. The extracts were dried and concentrated. The residue was dissolved in ethyl acetate and product was crystallized out to provide *tert*-butyl 2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethylcarbamate (0.158 g 0.41 mmol).

A suspension comprised of *tert*-butyl 2-benzylsulfonyl-1*R*-cyanomethylcarbamoyl-ethylcarbamate (5.22 g, 13.7 mmol) in anhydrous tetrahydrofuran (15 mL) was treated with methanesulfonic acid (1.8 mL, 27 mmol) and then the mixture was disluted with additional tetrahydrofuran (20 mL) and methanesulfonic acid (1.8 mL). The mixture was stirred for 16 hours and then diluted with diethyl ether. A resulting precipitate was collected by filtration to provide 2*R*-amino-3-benzylsulfonyl-*N*-cyanomethylpropionamide methanesulfonate salt (4.4 g, 11.6 mmol).

REFERENCE 6

3-Benzylsulfanyl-*N*-cyanomethyl-2*R*-isocyantopropionamide, a compound of Formula 4 in which $X^2$ is methylene, $R^1$ and $R^2$ are both hydrogen and $R^3$ is phenyl

A three necked round bottom flask with nitrogen inlet and exit to a 10% sodium hydroxide solution was charged with 2*R*-amino-3-benzylsulfanyl-

*N*-cyanomethylpropionamide *para*-toluenesulfonate salt (5 g, 11.8 mmol), prepared as in Reference 4, dichloromethane (120 mL), and saturated sodium bicarbonate solution (120 mL). The mixture was cooled in an ice bath and stirred for 10 minutes. The layers were allowed to separate and then a 20% solution of phosgene (12.4 mL, 23.6 mmol) in toluene was added to the lower layer. The mixture was stirred for 10 minutes. The aqueous phase was separated and extracted with dichloromethane. The combined organic phase was washed with brine, dried ($MgSO_4$), filtered, diluted with toluene (20 mL), concentrated and dried under high vacuum. The residue was dissolved in dichloromethane (15 mL) to provide a stock solution of 3-benzylsulfanyl-*N*-cyanomethyl-2*R*-isocyantopropionamide.

## REFERENCE 7

(*R*)-3-[2-(1,1-Difluoro-methoxy)-phenylmethanesulfonyl]-2-[(1-morpholin-4-yl-methanoyl)-amino]-propionic acid

A solution of (*R*)-2-*tert*-butoxycarbonylamino-3-((*R*)-2-*tert*-butoxycarbonylamino-2-carboxy-ethyldisulfanyl)-propionic acid (i.e., Boc-L-Cystine) (25 g, 56.75 mmol) in DMF (250 mL) was treated with tris(carboxyethyl)phosphine hydrochloride (17.9 g, 62.4 mmol). A solution of KOH (31.8 g, 567 mmol) in water (100 mL) was added over 2 minutes and the exothermic reaction was cooled with a 20°C water bath. The mixture was stirred for 2 hours at room temperature, diluted with 2-(difluoromethoxy)benzyl bromide and stirred for 2 hours. The mixture was acidified with 1N HCl and extracted with ethyl acetate (3 x 250mL). The combined organic layers were washed with brine, dried ($MgSO_4$)and concentrated. The residue was dried under high vacuum and then dissolved in $CH_2Cl_2$ (80 mL). The solution was diluted with trifluoroacetic acid (80 mL) and the mixture was stirred at room temperature for 2.5 hours. All volatile components were removed under vacuum and the residue was dissolved in water (200 mL). The solution was adjusted to pH 6 to 7 with 1N NaOH to give a precipitate, which was collected by filtration, washed with water and dried under vacuum to yield (*R*)-2-amino-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-propionic acid as white solid (27.5 g).

A mixture of (*R*)-2-amino-3-[2-(1,1-difluoro-methoxy)-benzylsulfanyl]-propionic acid (5 g, 18.03 mmol) and *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (8.5 mL, 45.8 mmol) was heated at 70°C under $N_2$ for 1 hour. All volatile reaction products were removed under vacuum. The residue was dissolved in $CH_2Cl_2$ (10 mL) and the solution treated with morpholinecarbonyl chloride (4.2 mL, 36 mmol). The mixture was stirred at room temperature for 16 hours and then diluted with ethyl acetate (300mL). The mixture was washed with water (50 mL) and brine (100 mL), dried ($MgSO_4$) and concentrated. The residue was dissolved in methanol (250 mL) and a saturated aqueous solution of Oxone® (35 g, 57 mmol) was added. The mixture was stirred at room temperature for 2 hours. The methanol was removed under vacuum and the remaining aqueous phase was extracted with ethyl acetate (3 x 200mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. The product was purified by flash chromatography on silica gel (Eluent: ethyl acetate to 10% methanol in ethyl acetate) to yield (*R*)-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-[(1-morpholin-4-yl-methanoyl)-amino]-propionic acid as colorless oil (6.5 g).

## REFERENCE 8

*N*-[2-*tert*-Butyldisulfanyl-1*R*-cyanomethylcarbamoylethyl]morpholine-4-carboxamide

A solution comprised of 2*R*-amino-3-*tert*-butyldisulfanylpropionic acid hydrate (25 g, 119 mmol) in sodium hydroxide (1N, 300 mL) was cooled to 0°C and then treated with 4-morpholinecarbonyl chloride (13.9 mL, 119 mmol) added slowly. The mixture was treated with additional amounts of sodium hydroxide (5N, 100 mL) and 4-morpholinecarbonyl chloride (27.8 mL, 238 mmol), stirred for approximately 12 hours and acidification with concentrated hydrochloric acid. Product was extracted with ethyl acetate and the combined extracts were washed with brine, dried ($MgSO_4$) and concentrated. The product was recrystallized from ethyl acetate/hexane, to provide 3-*tert*-butyldisulfanyl-2*R*-morpholin-4-ylcarbonylaminopropionic acid (16.5 g, 51.2 mmol) as a white crystalline solid.

A suspension of 3-*tert*-butyldisulfanyl-2*R*-morpholin-4-ylcarbonylaminopropionic

acid (16.25 g, 50.4 mmol) in methylene chloride (100 mL) was treated with EDCI (10.6 g, 55.4 mmol), HOBt (8.85 g, 65.5 mmol) and aminoacetonitrile hydrochloride (7.0 g, 75.6 mmol). The mixture then was treated with 4-methylmorpholine (8.31 mL, 75.6 mmol), stirred at ambient temperature for 5 hours and then diluted with ethyl acetate (500 mL). The dilution was washed with saturated aqueous sodium bicarbonate solution, brine, 1N hydrochloric acid and brine, dried ($MgSO_4$) and concentrated. Product was purified from the residue by flash chromatography on silica gel with ethyl acetate as eluent to provide *N*-[2-*tert*-butyldisulfanyl-1*R*-cyanomethylcarbamoylethyl]morpholine-4-carboxamide (7.5 g) as a white solid.

REFERENCE 9

2-(2-thienyl)aminoacetonitrile hydrochloride

A mixture of ammonium chloride (24.9g, 465 mmol) and 2-thiophenecarboxaldehyde (21.2 mL, 227mmol) in 250mL diethyl ether was treated with an 80mL aqueous solution of sodium cyanide (16.7g, 341 mmol) over 20 minutes. The mixture was allowed to stir for 16 hours. The aqueous layer was removed. The ether layer was washed (2 x 100mL) with saturation sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and concentrated. The residue was dissolved in 250 mL diethyl ether and cooled in an ice bath. Hydrogen chloride was bubbled through the solution until precipitation was complete. The salt was filtered and dried under reduced pressure to give 9.8g of 2-(2-thienyl)aminoacetonitrile hydrochloride.

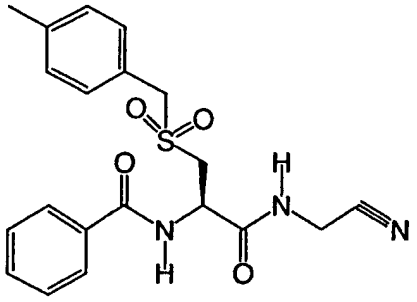
The following intermediate was provided by proceeding as in reference 9:

Amino-furan-2-yl-acetonitrile

EXAMPLE 1

*N*-[(*R*)-1-(Cyanomethyl-carbamoyl)-2-*p*-tolylmethanesulfonyl-ethyl]-benzamide

(Compound 1)



A mixture comprised of 2*R*-benzoylamino-3-(4-methylbenzylsulfanyl)propionic acid (1.316 g, 3.88 mmol), prepared as in Reference 1, EDCI (0.878 g, 5.56 mmol), HOBt (0.616 g, 4.56 mmol) and aminoacetonitrile bisulfate (0.726 g, 4.71 mmol) in *N*-methylpyrrolidinone (14 mL) and *N*-methylmorpholine (1 mL) was stirred at 25° C for 5 hours. The mixture then was diluted with cold 0.05 N aqueous hydrochloric acid and the product was extracted with ethyl acetate. The extracts were washed with aqueous sodium bicarbonate, dried and concentrated. The residue was dissolved in *tert*-butylmethyl ether and the product was crystallized from solution to provide *N*-[1*R*-cyanomethylcarbamoyl-2-(4-methylbenzylsulfanyl)ethyl]benzamide (0.86 g). Mass Spectrum: m/e 367.9 (theory 367.1). NMR Spectrum (DMSO): 8.82 (t, 1H), 8.69 (d, 1H), 7.88 (d, 2H), 7.5 (m, 3H), 7.16 (d, 2H), 7.08 (d, 2H), 4.7 (m, 1H), 4.2 (d, 2H), 3.7 (s, 2H), 2.75 (m, 2H), 2.1 (s, 3H) ppm.

A solution comprised of *N*-[1*R*-cyanomethylcarbamoyl-2-(4-methylbenzylsulfanyl)ethyl]benzamide (0.365 g, 0.99 mmol) in methanol (20 mL) was treated with Oxone® (1.03 g, 1.68 mmol) in water (20 mL) and the mixture was stirred at 25° C for 16 hours. The mixture then was diluted with cold water and the product was extracted with ethyl acetate. The extracts were dried and concentrated. The residue was dissolved in ethyl acetate and the product was crystallized from solution to provide *N*-[1*R*-cyanomethylcarbamoyl-2-(4-methylbenzylsulfonylsulfanyl)ethyl]benzamide (0.229 g 0.57 mmol).

The following compounds of Formula I were provided by proceeding as in Example 1:

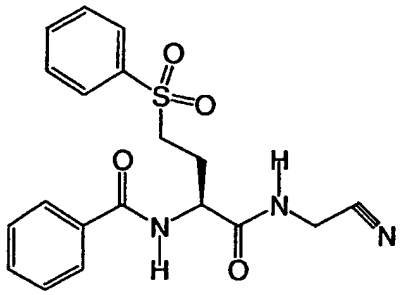
*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)benzamide (Compound 2); Mass Spectrum: m/e 386 (theory 385.4); NMR Spectrum (DMSO): δ: 8.98 (d, J = 9.4 Hz, 1H), 8.87 (t, J = 7 Hz, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.6 - 7.3 (m, 8H), 5.02 (m, 1H), 4.54 (s, 2H), 4.11 (m, 2H), 3.75 (m, 1H), 3.54 (dd, 1H), 3.29 (d, J = 5.6 Hz, 2H) ppm; and

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-methoxybenzylsulfonyl)ethyl]benzamide (Compound 3); Mass Spectrum: m/e 415.9 (theory 415.5); NMR Spectrum (DMSO): δ: 8.96 (d, 1H), 8.79 (t, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.6 - 7.4 (m, 3H), 7.30 (d, J = 10.3 Hz, 2H), 6.94 (d, J = 9.9 Hz, 2H), 5.02 (dd, J = 10.7 and 3.8 Hz,1H), 4.47 (AB q, J = 15.4 Hz, 2H), 4.13 (Br s, 2H), 3.75 (s, 3H), 3.72 (dd, J = 15.7 and 3.4 Hz, 1H), 3.50 (dd, J = 15.9 and 10.4 Hz, 1H) ppm.

## EXAMPLE 2

*N*-(3-Phenylsulfonyl-1*R*-cyanomethylcarbamoylpropyl)benzamide

(Compound 4)



A solution comprised of 2*R*-benzoylamino-4-phenylsulfanylbutyric acid (150 mg, 0.5 mmol), prepared as in Reference 2, in *N*-methylpyrrolidone (4 mL) was treated with HOBt (99 mg, 0.8 mmol), EDCI (125 mg, 0.65 mmol), *N*-methylmorpholine (1.5 mmol) and aminoacetonitrile bisulfate (115 mg, 0.75 mmol). The mixture was stirred 4 hours at ambient temperature and then diluted with cold water. Product was extracted with ethyl acetate and the extract was washed with dilute

hydrochloric acid and aqueous sodium bicarbonate, dried and then concentrated to provide *N*-(3-phenylsulfanyl-1*R*-cyanomethylcarbamoylpropyl)-benzamide (122 mg, 0.34 mmol).

A solution comprised of *N*-(3-phenylsulfanyl-1*R*-cyanomethylcarbamoylpropyl)-benzamide (122 mg, 0.34 mmol) in methanol (7 mL) was treated with Oxone® (317 mg, 1.1 mmol) in water (2 mL) and the mixture was stirred at ambient temperature for 6 hours. The reaction mixture was diluted with aqueous sodium chloride and product was extracted with ethyl acetate. The extract was dried and concentrated. The residue was dissolved in ethyl acetate and the product was crystallized from solution to provide *N*-(3-phenylsulfonyl-1*R*-cyanomethylcarbamoylpropyl)benzamide (122 mg, 0.31 mmol). Mass Spectrum: m/e 385.95 (theory 385.49). NMR Spectrum (DMSO): 8.70 (d, J = 9.4 Hz, 1H), 8.68 (t, J = 6.6 Hz, 1H), 7.95 - 7.45 (m, 10H), 4.45 (m, 1H), 4.13 (d, J = 6.1 Hz, 2H), 3.6 - 3.2 (m, 2H), 2.15 - 1.95 (m, 2H) ppm.

The following compounds were provided by proceeding as in Example 2:

Morpholine-4-carboxylic acid [(S)-1-(cyanomethyl-carbamoyl)-3-(2-trifluoromethoxy-benzenesulfonyl)-propyl]-amide (Compound 167) NMR $^1$H (DMSO, 300 MHz): 8.53 (t, 5.2Hz, 1H), 7.98 (d, 8.2Hz, 1H), 7.89 (t, 6.2 Hz, 1H), 7.65 (m, 2H), 6.78 (d, 8.2 Hz, 1H), 4.20 (m, 1H), 4.08 (d, 3.6 Hz, 2H), 3.55 (m, 4H), 3.40 (m, 2H), 3.24 (m, 4H), 1.98 (m, 1H), 1.82 (m, 1H); MS (M-1) = 476.2;

Morpholine-4-carboxylic acid [(S)-3-benzenesulfonyl-1-(cyanomethyl-carbamoyl)-propyl]-amide (Compound 168) NMR $^1$H,(DMSO, 300 MHz) 8.50 (t, 5.1 Hz, 1H), 7.88 (d, 7.1 Hz, 2H), 7.75 (m, 1H), 7.65 (t, 7.1 Hz, 2H), 4.18 (m, 1H), 4.10 (d, 3.5 Hz, 2H), 3.50 (m, 4H), 3.35 (m, 2H), 3.21 (m, 4H), 1.75-2.05 (m, 2H);

Morpholine-4-carboxylic acid [(S)-1-(cyanomethyl-carbamoyl)-3-(4-trifluoromethoxy-benzenesulfonyl)-propyl]-amide (Compound 169) NMR $^1$H,(DMSO, 300 MHz) 8.55 (t, 5.9 Hz, 1H), 8.04 (d, 8.9 Hz, 2H), 7.45 (d, 8.9 Hz, 2H), 7.72 (d, 8.1 Hz, 1H), 4.20 (m, 1H), 4.08 (d, 3.7,Hz, 2H), 3.53 (m, 4H), 3.20-3.45 (m, 6H), 1.75-2.05 (m, 2H); MS (M+1) = 479.0;

Thiophene-2-carboxylic acid [(S)-1-(cyanomethyl-carbamoyl)-3-(2-trifluoromethoxy-benzenesulfonyl)-propyl]-amide (Compound 170) NMR $^1$H: (DMSO,

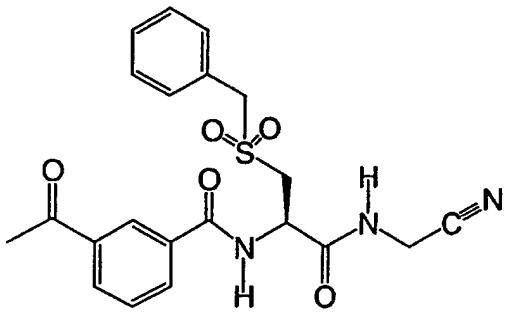
300 MHz) 8.74 (m, 1H), 7.95 (d, 8.8.Hz, 2H), 7.88 (m, 1H), 7.80 (m, 3H), 7.65 (m, 2H), 4.50 (m, 1H), 4.12 (d, 3.6 Hz, 2H), 3.40 (m, 2H), 2.12 (m, 1H), 1.90 (m, 1H); MS (M-1) = 474.0;

[(S)-1-(Cyanomethyl-carbamoyl)-3-(2-trifluoromethoxy-phenylsulfanyl)-propyl]-carbamic acid *tert*-butyl ester (Compound 171) MS (M+1) = 465.8;

EXAMPLE 3

3-Acetyl-*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)benzamide

(Compound 5)



A mixture comprised of 2*R*-amino-3-benzylsulfanyl-*N*-cyanomethylpropionamide *para*-toluenesulfonate salt (845 mg, 2 mmol), prepared as in Reference 4, EDCI (423 mg, 2.2 mmol), HOBt (459 mg, 3 mmol), 3-acetylbenzoic acid (328 mg, 2 mmol) and anhydrous dichloromethane (1.5 mL) was treated with *N*-methylmorpholine (0.485 mL, 4.4 mmol), stirred for 16 hours and then diluted with ethyl acetate. The mixture was washed with water, 1 N hydrochloric acid, water, sodium bicarbonate solution, water and brine, dried ($MgSO_4$), filtered and concentrated. The residue was stirred vigorously in diethyl ether and a resulting precipitate was collected by filtration and dried under high vacuum to provide 3-acetyl-*N*-(2-benzylsulfanyl-1*R*-cyanomethylcarbamoylethyl)benzamide (420 mg, 1.1 mmol).

A solution comprised of 3-acetyl-*N*-(2-benzylsulfanyl-1*R*-cyanomethylcarbamoyl-ethyl)benzamide 0.198 g, 0.5 mmol) in methanol (8 mL) was treated with Oxone® (0.46 g, 0.75 mmol) in water (8 mL) and the reaction mixture was

stirred at 25°C for 16 hours. The reaction mixture then was diluted with cold water and the product was extracted with ethyl acetate. The extracts were dried and concentrated. The residue was dissolved in ethyl acetate and the product was crystallized from solution to provide 3-acetyl-*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)benzamide (0.169 g 0.395 mmol). Mass Spectrum: m/e $m^+$ 428.0, $m^+$ 426.2; NMR Spectrum ($CD_3OD$): 8.49 (m, 1H), 8.16 (m, 1H), 8.09 (m, 1H), 7.61 (m, 1H), 7.45 (m, 2H), 7.37 (m, 3H), 5.21 (dd, J = 3.96, 11.14 Hz, 1H), 4.50 (m, 2H), 4.17 (d, J = 1.24 Hz, 2H), 3.88 (dd, J = 3.96, 15.93 Hz, 1H), 3.54 (dd, J = 9.15, 16.23 Hz, 1H).

The following compounds of Formula I were provided by proceeding as in Example 3:

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)naphthalene-2-carboxamide (Compound 6); Mass Spectrum: m/e 435.83; NMR Spectrum ($CDCl_3$): 8.30 (s, 1H), 7.81 (m, 5H), 7.49 (m, 2H), 7.33 (m, 5H), 5.16 (m, 1H), 4.34 (d, J = 2.7 Hz, 2H), 4.09 (s, 2H), 3.55 (m, 2H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)furan-3-carboxamide (Compound 7); Mass Spectrum: m/e 375.80; NMR Spectrum ($CDCl_3$): 8.00 (m, 1H), 7.45 (m, 3H), 7.40 (m, 4H), 6.65 (m, 1H), 5.10 (m, 1H), 4.41 (m, 2H), 4.14 (m, 2H), 3.70 (m, 1H), 3.31 (m, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)benzo[1,3]dioxole-5-carboxamide (Compound 8); Mass Spectrum: m/e 429.85; NMR Spectrum ($CDCl_3$): 7.32 - 7.43 (m, 6H), 7.26 (d, J = 1.92Hz), 6.79 (d, J = 7.92 Hz, 1H), 5.99 (s, 2H), 5.10 (dd, J = 6.87, 10.02 Hz, 1H), 4.35 (m, 2H), 4.09 (m, 2H), 3.60 (dd, J = 6.44, 15.20 Hz, 1H), 3.42 (dd, J = 5.45, 16.47Hz, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)-3-pyrid-3-ylacrylamide (Compound 9); Mass Spectrum m/e $m^+$ 412.76; $^1$H-NMR (300MHz, $CDCl_3$, δ ppm), 8.78 (m, 1H), 8.53 (m, 1H), 7.88 (m, 1H), 7.58 (d, J = 18Hz, 1H), 7.36 (m, 6H), 6.63 (m, 1H), 5.08 (m, 1H), 4.36 (m., 2H), 4.10 (d, J = 5.8Hz, 2H), 3.48 (m, 2H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)benzofuran-2-carboxamide (Compound 10); Mass Spectrum: m/e 425.83; NMR Spectrum ($CD_3OD$): 7.35 (m, 1H),

7.60 (m, 1H), 7.55 (m, 1H), 7.44 - 7.50 (m, 3H), 7.29 - 7.39 (m, 4H), 5.23 (dd, J = 4.21, 6.44 Hz, 1H), 4.50 (s, 2H), 4.16 (d, J = 1.98 Hz), 3.87 (dd, J = 4.21, 16.5 Hz), 3.58 (dd, J = 8.66, 16.5 Hz);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)furan-2-carboxamide (Compound 11); Mass Spectrum: m/e 375.80; NMR Spectrum ($CD_3OD$): 7.69 (dd, J = 0.74, 1.73 Hz, 1H), 7.44 (m, 2H), 7.37 (m, 4H), 7.18 (dd, J = 0.74, 2.72 Hz, 1H), 6.61 (dd, J = 1.72, 2.60 Hz, 1H), 5.14 (dd, J = 4.21, 6.31 Hz, 1H), 4.48 (s, 2H), 4.15 (d, J = 1.98 Hz, 2H), 3.82 (dd, J = 4.21, 14.85 Hz, 1H), 3.52 (dd, J = 8.42, 14.61 Hz, 1H);

*tert*-butyl 2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethylcarbamate (Compound 12); Mass Spectrum: m/e 381.84; NMR Spectrum (DMSO): δ: 8.78 (t, J = 5.20Hz, 1H), 7.43 (m, 6H), 4.58 (dd, J = 2.97, 8.16 Hz, 1H), 4.52 (s, 2H), 4.13 (dd, J = 3.22, 5.44 Hz, 2H), 3.59 (dd, J = 3.46, 7.18 Hz, 1H), 3.33 (m, 1H, under $H_2O$), 1.40 (s, 9H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)-3-phenoxybenzamide (Compound 13); Mass Spectrum: m/e: $m^+$ 477.8, $m^-$ 476.2; NMR Spectrum ($CDC1_3$): 7.62 (m, 1H), 7.3 - 7.54 (M, 11H), 7.15 (m, 1H), 7.00 (m, 1H), 5.16 (dd, J = 5.69, 12.62 Hz, 1H), 4.47 (m, 2H), 4.11 (m, 2H), 3.70 (dd, J = 5.44, 15.09 Hz, 1H), 3.33 (dd, J = 5.69, 16.20 Hz, 1H);

*tert*-butyl [3-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethylcarbamoyl)benzyl)-carbamate (Compound 14); Mass Spectrum: m/e $m^+$ 414.8, $m^-$ 513.2; NMR Spectrum ($CD_3OD$): 7.75 (m, 2H), 7.39 (m, 8H), 5.20 (dd, J = 3.96, 8.16 Hz, 1H), 4.48 (s, 2H), 4.24 (s, 2H), 4.13 (m, 2H), 3.85 (dd, J = 9.36, 16.23 Hz, 1H), 3.55 (dd, J = 9.90, 16.20 Hz, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)-4-hydroxybenzamide (Compound 15); Mass Spectrum: m/e $m^+$ 401.8, $m^-$ 400.0; NMR Spectrum (DMSO): δ: 8.75 (m, 1H), 7.76 (d, J = 8.66 Hz, 2H), 7.39 (s, 5H), 6.84 (d, J = 8.66 Hz, 2H), 5.02 (m, 1H), 4.55 (s, 2H), 4.13 (m, 2H), 3.77 (m, 1H), 3.53 (m, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)-3-hydroxybenzamide (Compound 16); Mass Spectrum: m/e $m^+$ 402.0, $m^-$ 400.0; NMR Spectrum ($CD_3OD$): 7.68 (m, 1H), 7.40 (m, 8H), 5.16 (dd, J = 4.21, 9.15 Hz, 1H), 4.50 (s, 2H), 4.16 (s, 2H), 3.84 (dd, J = 3.96, 16.20 Hz, 1H), 3.55 (dd, J = 8.91, 21.99 Hz, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)thiophene-2-carboxamide (Compound 17); Mass Spectrum m/e: $m^+$ 392.2, $m^-$ 390.2; NMR Spectrum (DMSO): δ: 9.04 (d, J = 8.16 Hz, 1H), 8.87 (m, 1H), 7.81 (m, 2H), 7.39 (m, 5H), 7.19 (m, 1H), 5.01 (m, 1H), 4.56 (s, 2H), 4.14 (m, 2H), 3.77 (dd, J = 3.46, 16.23 Hz), 3.51 (dd, J = 9.15, 15.93 Hz);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)thiophene-3-carboxamide (Compound 18); Mass Spectrum: m/e $m^+$ 392.0, $m^-$ 390.2; NMR Spectrum (DMSO): δ: 8.58 (m, 2H), 8.19 (dd, J = 0.99, 4.95 Hz, 1H) 7.62 (m, 1H), 7.53 (dd, J = 0.99, 4.95 Hz, 1H), 7.39 (s, 5H), 5.01 (m, 1H), 4.56 (s, 2H), 4.14 (d, J = 5.44 Hz, 2H), 3.76 (dd, J = 3.46, 12.87 Hz, 1H), 3.51 (dd, J = 9.40, 14.60 Hz, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)quinoline-3-carboxamide (Compound 19); Mass Spectrum: m/e $m^+$ 436.89; $^1$H-NMR (300MHz, $CDCl_3$, δ ppm): 9.20 (m, 1H), 8.77 (m, 1H), 8.02 (t, J = 9.5Hz, 2H), 7.84 (t, J = 7.3Hz, 1H), 7.65 (t, J = 7.3Hz, 1H), 7.43 (m, 2H), 7.34 (m, 3H), 5.23 (m, 1H), 4.18 (m, 2H), 3.83 (m, 1H), 3.46 (m, 1H);

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)biphenyl-4-ylcarboxamide (Compound 20); NMR Spectrum (DMSO): δ: 9.05 (d, J = 8.17 Hz, 1H), 8.82 (t, J = 5.69 Hz, 1H), 7.98 (m, 2H), 7.76 (m, 4H), 7.49 (m, 2H), 7.36 (m, 6H), 5.09 (m, 1H), 4.56 (s,2H), 4.14 (m, 2H), 4.04 (m, 2H), 3.79 (m, 1H), 3.58 (m, 1H);

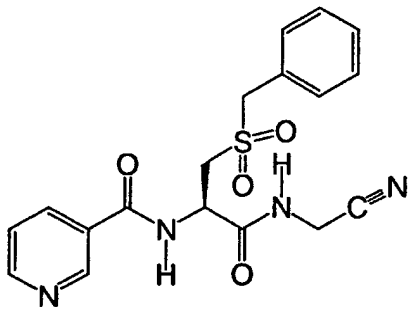
*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)quinoline-2-carboxamide (Compound 21); Mass Spectrum m/e $m^+$ 436.2, $m^-$ 435.0, $^1$H-NMR (300MHz, DMSO-$d_6$, δ ppm) 9.51 (d, J = 9.6Hz, 1H), 8.84 (t, J = 6.6Hz, 1H), 8.63 (d, J = 9.33Hz, 1H), 8.19 (m, 3H), 7.90 (m, 1H), 7.75 (m, 1H), 7.38 (m, 5H), 5.18 (m, 1H), 4.58 (dd, J = 15.1Hz, 19.4Hz, 2H), 4.14 (d, J = 6.3Hz, 2H) 3.81 (d, 6.6Hz, 2H); and

4-benzoyl-*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)benzamide (Compound 22); Mass Spectrum: m/e $m^+$ 490.4, $m^-$ 488.2; NMR Spectrum (DMSO): δ: 9.24 (m, 1H), 8.87 (m, 1H), 8.04 (d, J = 8.41 Hz, 2H), 7.85 (d, J = 8.41 Hz, 2H), 7.75 (m, 3H), 7.59 (m, 2H), 7.41 (s, 5H), 5.10 (m, 1H), 4.60 (s, 2H), 4.16 (m, 2H), 3.81 (m, 1H), 3.57 (m, 1H).

EXAMPLE 4

*N*-(2-Benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)nicotinamide

(Compound 23)



A mixture comprised of 2*R*-amino-3-benzylsulfonyl-*N*-cyanomethylpropionamide methanesulfonate salt (377 mg, 1 mmol), prepared as in Reference 5, EDCI (211 mg, 1.1 mmol), HOBt (230 mg, 1.5 mmol), nicotinic acid (123 mg, 1 mmol), and anhydrous dichloromethane (4 mL) was treated with *N*-methylmorpholine (0. 242mL, 2.2 mmol), stirred for 16 hours and then concentrated. The residue was partitioned between ethyl acetate (150 mL) and water (10 mL) and the ethyl acetate layer was separated and washed with 1 N hydrochloric acid, water, sodium bicarbonate solution, water and brine, dried ($MgSO_4$), filtered and concentrated. The residue was stirred vigorously in diethyl ether and a resulting precipitate was collected by filtration and dried under high vacuum to provide *N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)nicotinamide (236 mg, 0.61 mmol). Mass Spectrum: m/e 387.04. NMR Spectrum (DMSO): δ: 9.23 (d, J = 7.92 Hz, 1H), 9.04 (s, 1H), 8.89 (m, 1H), 8.75 (m, 1H), 8.21 (d, J = 7.18 Hz, 1H), 7.56 (m, 1H), 7.40 (s, 5H), 5.08 (m, 1H), 4.60 (s, 2H), 4.16 (m, 2H), 3.82 (m, 1H), 3.54 (m, 1H).

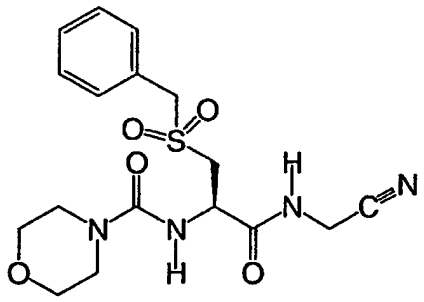
Proceeding as in Example 4 provided *N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)isonicotinamide (Compound 24); Mass Spectrum: m/e $m^+$ 386.6, $m^-$ 385.2; NMR Spectrum (DMSO): δ: 9.32 (d, J = 7.92 Hz, 1H), 8.90 (m, 1H), 8.79 (m, 2H), 7.80 (m, 2H), 7.42 (s, 5H), 5.08 (m, 1H), 4.60 (s, 2H), 4.17 (m, 2H), 3.83

(m, 1H), 3.56 (m, 1H);

EXAMPLE 5

*N*-(2-Benzylsulfonyl-1*R*-cyanomethylcarbamoylethylmorpholine-4-carboxamide

(Compound 25)



A solution comprised of 2*R*-amino-3-benzylsulfanyl-*N*-cyanomethylpropionamide *para*-toluenesulfonate salt (15 g, 35.5 mmol), prepared as in Reference 4, in anhydrous dichloromethane (200 mL) was cooled in an ice bath and then treated with morpholin-4-ylcarbonyl chloride (5.8 mL, 49.7 mmol) and *N*-methylmorpholine (11.7 mL, 106.5 mmol). The mixture was stirred at ambient temperature for 16 hours and then diluted with dichloromethane (400 mL). The dilution was washed with water, 1 N hydrochloric acid, water, sodium bicarbonate solution, water and brine, dried ($MgSO_4$), filtered and concentrated. Product was purified from the residue by elution on silica gel chromatography using dichloromethane followed by 1:1 dichloromethane : ethyl acetate. The purified product was stirred vigorously under ethyl acetate and diethyl ether and a resulting precipitate was collected by filtration to provide *N*-(2-benzylsulfanyl-1*R*-cyanomethylcarbamoylethyl-morpholine-4-carboxamide (8.5 g, 23.1 mmol).

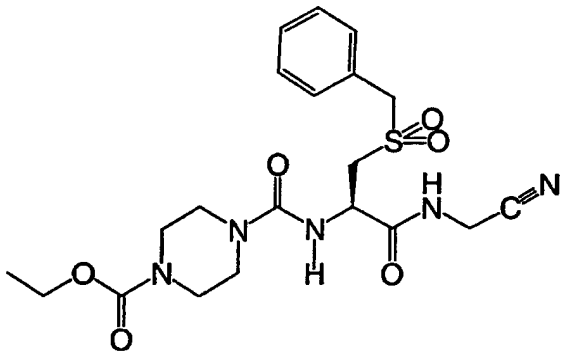
A solution comprised of *N*-(2-benzylsulfanyl-1*R*-cyanomethylcarbamoylethyl-morpholine-4-carboxamide (6 g, 16.5 mmol) in methanol (460 mL) was treated with Oxone® (15.3 g, 24.8 mmol) in water (460 mL) and the reaction mixture was stirred at 25° C for 30 minutes. The reaction mixture then was diluted with cold water and the product was extracted with ethyl acetate. The extracts were dried and concentrated.

The residue was dissolved in ethyl acetate and the product was crystallized from solution to provide *N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethylmorpholine-4-carboxamide (3.76 g 9.53 mmol). Mass Spectrum: m/e 394.91; NMR Spectrum (DMSO): δ: 8.67 (t, J = 5.45 Hz, 1H); 7.39 (m, 5H), 7.12 (d, J = 8.17 Hz, 1H), 4.72 (td, J = 9.33 Hz, 3.71 Hz, 1H), 4.51 (s, 2H), 4.12 (d, J = 5.69 Hz, 2H), 3.61 (dd, J = 3.71, 15.9 Hz, 1H), 3.55 (t, J = 4.70 Hz, 4H), 3.39 (dd, J = 9.16, 15.9 Hz, 1H), 3.30 (m, 4H).

Proceeding as in Example 5 provided *N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)-3-methoxybenzamide (Compound 26); Mass Spectrum: m/e 415.77; NMR Spectrum ($CDCl_3$): 7.31 - 7.44 (m, 10H), 7.04 (m, 1H), 5.12 (m, 1H), 4.38 (dd, J = 7.9, 14.0 Hz, 2H), 4.11 (m, 2H), 3.81 (s, 3H), 3.63 (dd, J = 6.19, 11.76 Hz, 1H); 3.40 (dd, J = 5.45, 14.86 Hz, 1H).

## EXAMPLE 6

Ethyl 4-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethylcarbamoyl)piperazine-1-carboxylate (Compound 27),



A stock of 3-benzylsulfanyl-*N*-cyanomethyl-2*R*-isocyantopropionamide (3 mL), prepared as in Reference 6, was diluted with dichloromethane (20 mL) and the mixture was treated with *N*-ethoxycarbonylpiperazine (0.69 mL, 2 mmol) and stirred for 16 hours. The mixture then was concentrated and partitioned between ethyl acetate and water. The organic phase was washed with water, 1 N hydrochloric acid, water, sodium

bicarbonate solution, water and brine, dried ($MgSO_4$), filtered and concentrated. Product was purified from the residue by elution on silica gel chromatography using 5% methanol in dichloromethane to provide ethyl 4-(2-benzylsulfanyl-1*R*-cyanomethylcarbamoylethyl-carbamoyl)piperazine-1-carboxylate (382 mg, 0.65 mmol).

A solution comprised of ethyl 4-(2-benzylsulfanyl-1*R*-cyanomethylcarbamoylethyl-carbamoyl)piperazine-1-carboxylate (0.187 g, 0.43 mmol) in methanol (4 mL) was treated with Oxone® (0.396 g, 0.65 mmol) in water (4 mL) and the reaction mixture was stirred at 25° C for 3 hours. The reaction mixture then was diluted with cold water and the product was extracted with ethyl acetate. The extracts were dried and concentrated. The residue was dissolved in ethyl acetate and the product was crystallized from solution to provide ethyl 4-2-enzylsulfonyl-1*R*-cyanomethylcarbamoylethylcarbamoyl)piperazine-1-carboxylate (0.159 0.34 mmol). Mass Spectrum: m/e $m^+$ 466.0, $m^-$ 464.2. NMR Spectrum (DMSO): δ: 8.67 (t, J = 5.44, Hz, 1H), 7.40 (s, 5H), 7.18 (d, J = 7.92 Hz, 1H), 4.74 (m, 1H), 4.53 (m,2H), 4.13 (m, 2H), 4.06 (q, J = 6.93 Hz, 2H), 3.66 (m, 1H), 3.44 (m, 1H), 3.35 (m, 8H), 1.19 (t, J = 6.93, Hz, 3H).

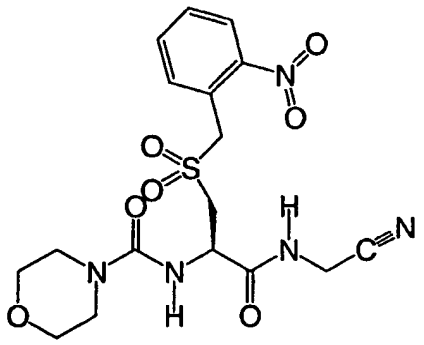
The following compounds of Formula I were provided by proceeding as in Example 6:

*tert*-butyl 4-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethylcarbamoyl)piperazine-1-carboxylate (Compound 28); Mass Spectrum: m/e $m^+$ 493.8, $m^-$ 492.2; NMR Spectrum (DMSO): δ: 8.66 (m, 1H), 7.40 (s, 5H), 7.17 (m, 1H), 4.73 (m, 1H), 4.52 (s, 2H), 4.13 (m, 2H), 3.62 (m, 1H), 3.24 - 3.48 (m, 9H), 1.41 (s, 9H); and

*N*-(2-benzylsulfonyl-1*R*-cyanomethylcarbamoylethyl)-4-fur-2-ylcarbonylpiperazine-1-carboxamide (Compound 29); Mass Spectrum: m/e $m^+$ 488.4, $m^-$ 486.2; NMR Spectrum (DMSO): δ: 8.69 (t, J = 5.44 Hz, 1H), 7.86 (m, 1H), 7.40 (s, 5H), 7.03 (d, J = 3.22 Hz, 1H), 6.64 (dd, J = 1.73, 1.73 Hz, 1H), 4.74 (m, 1H), 4.54 (s, 2H), 4.14 (d, J = 5.44 Hz, 2H), 3.67 (m, 4H), 3.45 (m, 4H).

EXAMPLE 7

*N*-[1*R*-Cyanomethylcarbamoyl-2-(2-nitrobenzylsulfonyl)ethyl]morpholine-4-carboxamide (Compound 30),



A mixture comprised of *N*-(2-*tert*-butyldisulfanyl-1*R*-cyanomethylcarbamoyl-ethyl)morpholine-4-carboxamide (560 mg, 1.6 mmol), provided as in Reference 8, tris-carboxyethyl phosphine (550 mg, 1.9 mmol) and DMF (4.5 mL) was treated with 4M aqueous potassium hydroxide (2 mL) with stirring at 23° C. The mixture was stirred for 3 hours under a nitrogen atmosphere and then treated with 2-nitrobenzyl bromide (830 mg, 3.8 mmol). The mixture was stirred for 16 hours and then diluted with ethyl acetate (200 ml). The organic phase was separated, sequentially washed with brine, saturated sodium bicarbonate and brine, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in 1:1 ethyl acetate/hexane and product was crystallized from solution to provide *N*-[1*R*-cyanomethylcarbamoyl-2-(2-nitrobenzylsulfanyl)ethyl]morpholine-4-carboxamide (478 mg) as a colorless solid. Mass Spectrum: m/e 399.2 (theory 398). NMR Spectrum (DMSO-$d_6$) δ 8.79 (t, J = 5.1 Hz, 1H), 8.69 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.58 - 7.65 (m, 2H), 7.43-7.55 (m, 4H), 4.62 (ddd, J = 13.6, 9.2, 5.1 Hz, 1H), 4.12 (d, J = 5.5 Hz, 2H), 4.06 (d, J = 3.0 Hz, 2H), 2.87 (dd, J = 13.5, 5.1, 1H), 2.76 (dd, J = 13.6, 9.5 Hz, 1H).

A solution comprised of *N*-[1*R*-cyanomethylcarbamoyl-2-(2-nitrobenzylsulfanyl)-ethyl]morpholine-4-carboxamide (50 mg, 0.13 mmol) in methanol (5 mL) was treated with Oxone® (105 g, 0.17 mmol) in water (1 mL) and the

reaction mixture was stirred at 25° C for 16 hours. The reaction mixture then was diluted with cold water and the product was extracted with ethyl acetate. The extracts were dried and concentrated. The residue was dissolved in ethyl acetate and product was crystallized from solution to provide *N*-[1*R*-cyanomethylcarbamoyl-2-(2-nitrobenzylsulfonyl)ethyl]morpholine-4-carboxamide (45 g, 0.1 mmol). Mass Spectrum: m/e 431 (theory 430). NMR Spectrum (DMSO-$d_6$) δ 8.99 (d, 1H, J = 8.1 Hz), 8.83 (t, J = 5.1 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 7 Hz, 1H), 7.64-7.69 (m, 2H), 7.46 - 7.61 (m, 3H), 5.08 (s, 2H), 5.03 (t, J = 6.6 Hz, 1H), 4.13 (s, 2H), 3.83 (d, J = 14.3 Hz, 1H), 3.66 (dd, J = 14.3, 9.9 Hz, 1H).

The following compounds of Formula I were provided by proceeding as in Example 7:

*N*-[2-(4-chlorobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 31); EI MS (M+ = 420.0); NMR (DMSO): δ 8.96 (d, 1H, J = 8.1 Hz), 8.79 (t, 1H, J = 5.5Hz), 7.87 (d, 2H, J = 6.2Hz), 7.39 - 7.56 (m, 7H), 5.03 (t, 1H, J = 6.6 Hz), 4.59 (s, 2H), 4.12 (d, 2H, J = 5.5Hz), 3.78 (dd, 1H, J = 14.3, 2.9Hz), 3.54 (dd, 1H, J = 14.3, 9.9 Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-methylbenzylsulfonyl)ethyl]benzamide (Compound 32); EI MS (M+ = 400.2); NMR (DMSO): δ 9.04 (d, 1H, J = 8.2 Hz), 8.85 (t, 1H, J = 5.4Hz), 7.90 (d, 2H, J = 8.4 Hz), 7.47 - 7.61 (m, 3H), 7.18 - 7.34 (m, 4H), 5.11 (t, 1H, J = 9.7 Hz), 4.65 (d, 1H, J = 13.6 Hz), 4.57 (d, 1H, J = 13.6 Hz), 4.16 (d, 2H, J = 5.9 Hz), 3.87 (dd, 1H, J = 14.3, 3.2 Hz), 3.68 (dd, 1H, J = 14.6, 9.6 Hz), 2.33 (s, 3H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3,5-dimethylbenzylsulfonyl)ethyl]benzamide (Compound 33); EI MS (M+ = 414.0); NMR (DMSO): δ 9.01 (d, 1H, J = 7.9 Hz), 8.81 (t, 1H, J = 5.7 Hz), 7.90 (d, 2H, J = 6.7 Hz), 7.48 - 7.61 (m, 3H), 7.00 (s, 1H), 6.98 (s, 2H), 5.04 (t, 1H, J = 11.4 Hz), 4.46 (s, 2H), 4.14 (d, 2H, J = 5.4Hz), 3.76 (dd, 1H, J = 14.6, 3.0 Hz), 3.53 (dd, 1H, J = 14.3, 9.4 Hz), 2.25 (s, 6H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-trifluoromethylbenzylsulfonyl)ethyl]benzamide (Compound 34); EI MS (M+ = 454.0);

NMR (DMSO): δ 8.99 (d, 14, J = 8.2 Hz), 8.81 (t, 1H, J = 5.7 Hz), 7.88 (d, 2H, J = 6.7 Hz), 7.79 (d, 2H, J = 8.2 Hz), 7.64 (d, 2H, J = 8.2 Hz), 7.48 - 7.58 (m, 3H), 5.08 (t, 1H, J = 8.8 Hz), 4.74 (s, 2H), 4.14 (d, 2H, J = 6.2 Hz), 3.84 (dd, 1H, J = 14.9, 3.5 Hz), 3.60 (dd, 1H, J = 14.3, 9.6 Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-trifluoromethoxybenzylsulfonyl)ethyl]benzamide (Compound 35); EI MS (M+ = 470.2); NMR (DMSO): δ 9.00 (d, 1H, J = 8.24 Hz), 8.82 (t, 1H, J = 5.6 Hz), 7.89 (d, 2H, J = 9.7 Hz), 7.40 - 7.58 (m, 7H), 5.04 - 5.11 (m, 1H), 4.65 (s, 2H), 4.15 (s, 1H), 3.82 (dd, 1H, J = 14.3, 3.2Hz), 3.59 (dd, 1H, J = 12.0, 9.7 Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-trifluoromethylsulfanylbenzylsulfonyl)ethyl]-benzamide (Compound 36); EI MS (M+ = 486.2); NMR (DMSO): δ 9.02 (d, 1H, J = 7.9 Hz), 8.82 (t, 1H, J = 5.7 Hz), 7.89 (d, 2H, J = 8.4 Hz), 7.76 (d, 2H, J = 8.2 Hz), 7.47 - 7.61 (m, 5H), 5.07 (t, 1H, J = 9.4 Hz), 4.70 (s, 2H), 4.15 (d, 2H, J = 5.7 Hz), 3.84 (dd, 1H, J = 14.6, 3.5 Hz), 3.61 (dd, 1H, J = 14.1, 94. Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-nitrobenzylsulfonyl)ethyl]benzamide (Compound 37); EI MS (M+ = 431.0); NMR (DMSO): δ 8.99 (d, 1H, J = 8.0 Hz), 8.82 (t, 1H, J = 5.7 Hz), 8.32 (s, 1H), 8.27 (d, 1H, J = 8.2 Hz), 7.88 (m, 3H), 7.73 (t, 1H, J = 3.1 Hz), 7.47 - 7.60 (m, 3H), 5.06 (t, 1H, J = 11.1 Hz), 4.82 (s, 2H), 4.14 (s, 2H), 3.86 (dd, 1H, J = 14.4, 3.2 Hz), 3.62 (dd, 1H, J = 14.6, 9.4 Hz);

*N*-(1*R*-cyanomethylcarbamoyl-2-pyrid-2-ylmethylsulfonylethyl)benzamide (Compound 38); Mass Spectrum: m/e 387.03 (theory 386.97); NMR Spectrum (DMSO): 9.01 (d, J = 9.1 Hz, 1H), 8.79 (t, J = 6.3 Hz, 1H), 8.57 (d, J = 4.4 Hz, 1H), 7.95 - 7.8 (m, 3H), 7.6 - 7.35 (m, 5H), 5.11 (m, 1H), 4.78 (d, J = 15.4 Hz, 1H), 4.69 (d, J = 15.4 Hz, 1H), 4.14 (d, J = 6.1 Hz, 2H), 3.86 (dd, J = 3.3 and 16 Hz, 1H), 3.65 (dd, J = 11 and 16 Hz, 1H) ppm;

*N*-(1*R*-cyanomethylcarbamoyl-2-pyrid-4-ylmethylsulfonylethyl)benzamide (Compound 39); Mass Spectrum: m/e 387.04 (theory 386.97); NMR Spectrum (DMSO): 8.99 (d, J = 9.1 Hz, 1H), 8.81 (t, J = 6.0 Hz, 1H), 8.60 (d, J = 6.6 Hz, 2H), 7.85 - 7.95 (m, 2H), 7.6 - 7.45 (m, 3H), 7.42 (d, J = 6.6 Hz, 2H), 5.00-5.15 (m, 1H),

4.67 (s, 2H), 4.13 (d, J = 6.6 Hz, 2H), 3.84 (dd, J = 3.9 and 16 Hz, 1H), 3.59 (dd, J = 16 and 10 Hz, 1H) ppm;

*N*-[1*R*-cyanomethylcarbamoyl-2-(3,4-dichlorobenzylsulfonyl)ethyl]benzamide (Compound 40); EI MS (M+ = 454.0); NMR (DMSO): δ 8.97 (d, 1H, J = 8.1 Hz), 8.80 (t, 1H, J = 5.9 Hz), 7.86 (d, 2H, J = 7.3 Hz), 7.66 - 7.70 (m, 2H), 7.46 - 7.58 (m, 4H), 5.04 (t, 1H, J = 7.3 Hz), 4.64 (t, 2H, J = 14.3 Hz), 4.13 (s, 2H), 3.81 (d, 1H, J = 14.7 Hz), 3.56 (dd, 1H, J = 14.3, 9.2 Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-methylbenzylsulfonyl)ethyl]benzamide (Compound 41); EI MS (M+ = 400.0); NMR (DMSO): δ 9.00 (d, 1H, J = 8.4 Hz), 8.81 (t, 1H, J = 5.7 Hz), 7.89 (d, 2H, J = 6.6 Hz), 7.47 - 7.59 (m, 3H), 7.25 (d, 1H, J = 6.2 Hz), 7.17 (brS, 3H), 5.02 - 5.06 (m, 1H), 4.51 (s, 2H), 4.13 (s, 2H), 3.76 (d, 1H, J = 14.3 Hz), 3.53 (dd, 1H, J = 13.2, 9.5 Hz), 2.28 (s, 3H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-nitrobenzylsulfonyl)ethyl]benzamide (Compound 42); NMR (DMSO): δ 8.98 (d, 1H, J = 7.7 Hz), 8.80 (t, 1H, J = 4.8 Hz), 8.25 (d, 2H, J = 6.6 Hz), 7.86 (d, 2H, J = 7.0 Hz), 7.67 (d, 2H, J = 7.0 Hz), 7.45 - 7.58 (m, 3H), 5.04 (t, 1H, 7.7 Hz), 4.80 (s, 2H), 4.12 (s, 2H), 3.84 (d, 1H, J = 16.8 Hz), 3.60 (dd, 1H, J = 13.6, 9.5 Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-nitrobenzylsulfonyl)ethyl]benzamide (Compound 43); EI MS (M+ = 431.2), Theory = 430; NMR (DMSO): δ 8.99 (d, 1H, J = 8.1 Hz), 8.83 (t, 1H, J = 5.1 Hz), 8.05 (d, 1H, J = 8.1 Hz), 7.86 (d, 2H, J = 8.1 Hz), 7.76 (d, 1H, J = 7.0 Hz), 7.64 - 7.69 (m, 2H), 7.46 - 7.61 (m, 3H), 5.08 (s, 2H), 5.03 (t, 1H, J = 6.6 Hz), 4.13 (s, 2H), 3.83 (d, 1H, J = 14.3 Hz), 3.66 (dd, 1H, J = 14.3, 9.9 Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-trifluoromethylbenzylsulfonyl)ethyl]benzamide (Compound 44); EI MS (M+ = 454.1), Theory = 453; NMR (DMSO): δ 8.98 (d, 1H, J = 7.3Hz), 8.79 (t, 1H, J = 5.1 Hz), 7.85 (d, 2H, J = 7.0 Hz0, 7.63 - 7.73 (M, 4H), 7.44 - 7.54 (m, 3H), 5.04 (t, 1H, J = 5.1 Hz), 4.71 (s, 2H), 4.11 (s, 2H), 3.81 (d, 1H, J = 13.9 Hz), 3.56 (dd, 1H, J = 13.9, 9.2. Hz);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-

trifluoromethoxybenzylsulfonyl)ethyl]benzamide (Compound 45); EI MS (M+ = 470.0), Theory = 469; NMR (DMSO): δ 9.00 (d, 1H, J = 8.1Hz), 8.81 (t, 1H, J = 5.9 Hz), 7.87 (d, 2H, J = 7.3 Hz), 7.40 - 7.56 (m, 7H), 5.05 (t, 1H, J = 5.9 Hz), 4.67 (s, 2H), 4.13 (d, 2H, J = 5.5 Hz), 3.81 (d, 1H, J = 14.3 Hz), 3.57 (dd, 1H, J = 14.3, 9.9 Hz);

*N*-(1*R*-cyanomethylcarbamoyl-2-pyrid-3-ylmethylsulfonylethyl)benzamide (Compound 46); Mass Spectrum: m/e 387.02 (theory 386.97); NMR Spectrum (DMSO): 8.99 (d, J = 9.1 Hz, 1H), 8.82 (t, J = 6.1 Hz, 1H), 8.62 - 8.54 (m, 2H), 7.94 - 7.8 (m, 3H), 7.62 - 7.4 (m, 4H), 5.12 - 5.0 (m, 1H), 4.66 (s, 2H), 4.14 (d, J = 6.6 Hz, 2H), 3.83 (dd, J = 3.9 and 16.2 Hz, 1H), 3.59 (dd, J = 10.7 and 16 Hz, 1H) ppm;

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-methylbenzylsulfonyl)ethyl]morpholine-4-carboxamide (Compound 47); Mass Spectrum: m/e 408.6 (theory 408.48); NMR Spectrum (DMSO): 8.70 (t, J = 6.0 Hz, 1H), 7.35 - 7.1 (m, 5H), 4.84 - 4.74 (m, 1H), 4.60 (d, J = 15 Hz, 1H), 4.52 (d, J = 15 Hz, 1H), 4.18 (d, J = 17 Hz, 1H), 4.10 (d, J = 17 Hz, 1H), 3.70 (dd, J = 3.8 and 15.9 Hz, 1H), 3.6 - 3.5 (m, 5H), 3.4 - 3.25 (m, 4H), 2.35 (s, 3H) ppm;

*N*-(1*R*-cyanomethylcarbamoyl)-2-pentafluorobenzylsulfonylethyl)benzamide (Compound 48); MS m/z = 476 (M+1); NMR (DMSO): δ 9.0 (d, J = 8 Hz, 1H), 8.8 (ddJ = 5.5, 3.6, 1H), 7.8 (dJ = 7.3, 2H), 7.5 (m, 3H), 4.8 (ddJ = 17, 6, 2H), 4.14 (s, 1H), 4.11 (s, 1H), 4.02 (s, 1H), 4.01 (s, 1H), 3.99 (dd, 3, 15, 1H), 3.78 (dd (10, 15, 1H) 5.0 (ddd, 3, 10, 8, 1H);

*N*-(1*R*-cyanomethylcarbamoyl-2-naphth-2-ylbenzylsulfonylethyl)benzamide (Compound 49); MS m/z = 436 (M+1); NMR (DMSO): δ 8.99 (d, 8 Hz, 1H), 8.8 (dd, 3,5,1H), 7.9 (m, 6H), 7.5 (m, 6H), 5.05 (m, 1H), 4.7 (s, 2H), 4.1 (d, 5, 2H), 3.8 (dd, 3,14, 1H), 3.55 (dd, 10, 14, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluorobenzylsulfonyl)ethyl]benzamide (Compound 50); Mass Spectrum: m/e 404.4 (theory 403.43); NMR Spectrum (DMSO): 9.00 (d, J = 9 Hz, 1H), 8.82 (t, J = 6.3 Hz, 1H), 7.93 - 7.82 (m, 2H),7.62 - 7.4 (m, 5H), 7.32 - 7.18 (m, 2H), 5.14 - 5.04 (m, 1H), 4.64 (s, 2H), 4.14 (d, J = 6.9 Hz, 2H), 3.84 (dd, J = 3.6 and 11.5 Hz, 1H), 3.67 (dd, J = 8.1 and 11 Hz, 1H) ppm;

*N*-[2-(2-chlorobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide

(Compound 51); Mass Spectrum: m/e 420.3 (theory 419.88); NMR Spectrum (DMSO): 9.17 (d, J = 9.1 Hz, 1H), 8.94 (t, J = 5.8 Hz, 1H), 7.98 - 7.9 (m, 2H), 7.6 - 7.32 (m, 7H), 5.15 - 5.05 (m, 1H), 4.75 (s, 2H), 4.14 (d, J = 6.3 Hz, 2H), 3.82 (d, J = 6.9 Hz, 2H) ppm;

*N*-(1*R*-cyanomethylcarbamoyl-2-prop-2-en-1-ylsulfonylethylbenzamide (Compound 52); Mass Spectrum: m/e 335.7 (theory 335.38); NMR Spectrum (DMSO): 9.00 (d, J = 8.1 Hz, 1H), 8.81 (t, J = 5.4 Hz, 1H), 7.89 (d, J = 7.4 Hz, 2H), 7.64 - 7.46 (m, 3H), 5.94 - 5.75 (m, 1H), 5.46 (d, J = 4.7 Hz, 1H), 5.41 (s, 1H), 5.06 - 4.95 (m, 1H), 4.13 (d, J = 5.7 Hz, 2H), 4.04 - 3.9 (m, 2H), 3.75 (dd, J = 3.2 and 14.6 Hz, 1H), 3.57 (dd, J = 9.4 and 14.6 Hz, 1H) ppm;

*N*-[2-(2-bromobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 53); Mass Spectrum: m/e 462.2 (theory 464.34); NMR Spectrum (DMSO): 9.03 (d, J = 8.2 Hz, 1H), 8.84 (t, J = 5.4 Hz, 1H), 7.90 (d, J = 6.9 Hz, 2H),7.75 - 7.25 (m, 7H), 5.17 - 5.05 (m, 1H), 4.75 (s, 2H), 4.15 (d, J = 5.7 Hz, 2H), 3.85 (dd, J = 3.4 and 14.1 Hz, 1H), 3.73 (dd, J = 14.6 and 9.4 Hz, 1H) ppm;

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-iodobenzylsulfonyl)ethyl]benzamide (Compound 54); Mass Spectrum: m/e 511.95 (theory 511.34); NMR Spectrum (DMSO): 9.02 (d, J = 9.1 Hz, 1H), 8.83 (t, J = 6.0 Hz, 1H), 7.94 - 7.88 (m, 3H), 7.6 - 7.37;

*N*-[2-(4-*tert*-butylbenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 55); Mass Spectrum: m/e 442.10 (theory 441.55); NMR Spectrum (DMSO): 8.99 (d, J = 9.1 Hz, 1H), 8.81 (t, J = 6.3 Hz, 1H), 7.94 - 7.85 (m, 2H), 7.62 - 7.44 (m, 3H), 7.41 (d, J = 9 Hz, 2H), 7.30 (d, J = 9 Hz, 2H), 5.1 - 5.02 (m, 1H), 4.51 (s, 2H), 4.13 (d, J = 6.6 Hz, 2H), 3.77 (dd, J = 3.9 and 16 Hz, 1H), 3.54 (dd, J = 7.8 and 16 Hz, 1H), 1.26 (s, 9H) ppm;

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-trifluoromethylbenzylsulfonyl)ethyl]benzamide (Compound 56); Mass Spectrum: M + 1 = 454; NMR 270 MHz (DMSO): 8.8 (m, 2H) 8.2 - 7.8 (m, 7H) 5.7 (ddd, 8,8,4, 1H) 5.2 (S,2H) 4.6 (DD, 5,3, 2H) 4.4 (dd 14, 4, 1H) 4.2 (dd 14, 8, 1H);

*N*-[1*R*-cyanomethylcarbamoyl)-2-(2-cyanobenzylsulfonyl)ethyl]benzamide (Compound 57); Mass Spectrum: M + 1 = 454; NMR 270 MHz. (acetone): 8 - 7.4 (m,

9H) 5.2 (m, 1H) 4.8 (S,2H) 4.2 (s, 2H) 4.0 (dd 14, 4, 1H) 3.8 (ddd 14, 9, 2,1H);

*N*-[2-(4-bromobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 58); Mass Spectrum: $(M+H^+)$ 464, 466; $(M-H^+)$ 462, 464;

*N*-[2-(3-chlorobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 59); Mass Spectrum: $(M+H^+)$ 420, 422; $(M-H^+)$ 418, 420; $^1H$ NMR: (DMSO) 8.98 (d, J=8.2Hz, 1H), 8.81 (t, J=6Hz, 1H), 7.88 (m, 2H), 7.60-7.35 (m, 7H), 5.05 (m, 1H), 4.62 (s, 2H), 4.14 (m, 2H), 3.81 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.56 (dd, , J=9.4Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-fluorobenzylsulfonyl)ethyl]benzamide (Compound 60); Mass Spectrum: $(M+H^+)$ 404; $(M-H^+)$ 402; $^1H$ NMR: (DMSO) 8.99 (d, J=7.9Hz, 1H), 8.81 (t, J=6Hz, 1H), 7.87 (m, 2H), 7.60-7.40 (m, 4H), 7.28-7.20 (m, 3H), 5.05 (m, 1H), 4.62 (s, 2H), 4.13 (m, 2H), 3.81 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.56 (dd, , J=9.4Hz, J=14.5Hz, 1H);

*N*-[2-(3-chloro-2-fluorobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 61); Mass Spectrum: $(M+H^+)$ 438, 440; $(M-H^+)$ 436, 438; $^1H$-NMR: (DMSO, δ) 9.00 (d, J = 8.4 Hz, 1H), 8.84 (t, J = 5.4Hz, 1H), 7.88 (d, J = 6.8 Hz, 2H), 7.65 - 7.42 (m, 5H), 7.28 (t, J = 7.7 Hz, 1H), 5.08 (m, 1H), 4.72 (s, 2H), 4.15 (m, 2H), 3.90 (dd, J = 3 Hz, J = 14.4 Hz, 1H), 3.70 (dd, J = 9.9 Hz, J = 14.4 Hz, 1H);

*N*-[1-cyanomethylcarbamoyl-2-(2-fluoro-3-methylbenzylsulfonyl)ethyl]benzamide (Compound 62); Mass Spectrum: $(M+H^+)$ 422; $(M-H^+)$ 420; $^1H$ NMR: (DMSO) 8.99 (d, J=7.9Hz, 1H), 8.81 (t, J=6Hz, 1H), 7.88 (m, 2H), 7.60-7.45 (m, 3H), 7.37-7.28 (m, 3H), 5.07 (m, 1H), 4.65 (s, 2H), 4.14 (m, 2H), 3.87 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.70 (dd, , J=9.4Hz, J=14.5Hz, 1H);

*N*-[1-cyanomethylcarbamoyl)-2-(2,5-difluorobenzylsulfonyl)ethyl]benzamide (Compound 63); Mass Spectrum: $(M+H^+)$ 422; $(M-H^+)$ 420; $^1H$-NMR: (DMSO, δ) 9.00 (d, J = 8.2 Hz, 1H), 8.84 (t, J = 5.6Hz, 1H), 7.87 (d, J = 8 Hz, 2H), 7.60 - 7.45 (m, 4H), 7.19 (t, J = 8 Hz, 1H), 5.10 (m, 1H), 4.68 (s, 2H), 4.15 (m, 2H), 3.90 (dd, J = 3.5 Hz, J = 14.4 Hz, 1H), 3.76 (dd, J = 9.9 Hz, J = 14.4 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl)-2-(4-iodobenzylsulfonyl)ethyl]benzamide (Compound 64); Mass Spectrum: $(M+H^+)$ 512; $(M-H^+)$ 510; $^1H$ NMR: (DMSO) 8.99

(d, J=7.9Hz, 1H), 8.81 (t, J=6Hz, 1H), 7.87 (m, 2H), 7.77 (d, J=8.2Hz, 2H), 7.57-7.46 (m, 3H), 7.19 (d, J=8.2Hz, 2H), 5.04 (m, 1H), 4.55 (s, 2H), 4.13 (m, 2H), 3.78 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.53 (dd, , J=9.4Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl)-2-(3-iodobenzylsulfonyl)ethyl]benzamide (Compound 65); Mass Spectrum: $(M+H^+)$ 512; $(M-H^+)$ 510; $^1$H NMR: (DMSO) 8.99 (d, J=8.2Hz, 1H), 8.80 (t, J=6Hz, 1H), 7.88 (m, 2H), 7.78-7.73 (m, 2H), 7.60-7.46 (m, 3H), 7.41 (d, J=7.7Hz, 1H), 7.20 (t, J=7.7Hz, 1H), 5.06 (m, 1H), 4.57 (s, 2H), 4.14 (m, 2H), 3.80 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.53 (dd, , J=9.9Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]benzamide (Compound 66); Mass Spectrum: $(M+H^+)$ 452; $(M-H^+)$ 450; $^1$H-NMR: (DMSO, δ) 8.99 (d, J = 8.2 Hz, 1H), 8.82 (t, J = 5.5Hz, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.60 - 7.44 (m, 5H), 7.29 (t, J = 5.5 Hz, 1H), 7.26 (t, J = 5.5 Hz, 1H) 7.13 (t, $J_{H,F}$ = 74Hz, 1H) 5.08 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.80 (dd, J = 2.7 Hz, J = 14.4 Hz, 1H), 3.76 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,5-dichlorobenzylsulfonyl)ethyl]benzamide (Compound 67); Mass Spectrum: $(M+H^+)$ 454, 456; $(M-H^+)$ 452, 454; $^1$H NMR: (DMSO) 9.02 (d, J=8.4Hz, 1H), 8.85 (t, J=5.4Hz, 1H), 7.89 (m, 2H), 7.61-7.46 (m, 6H), 5.11 (m, 1H), 4.76 (s, 2H), 4.15 (m, 2H), 3.88 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.73 (dd, , J=9.9Hz, J=14.5Hz, 1H);

*N*-[2-(3-bromobenzylsulfonyl)-1-cyanomethylcarbamoylethyl]benzamide (Compound 68); Mass Spectrum: $(M+H^+)$ 464, 466; $(M-H^+)$ 462, 464; $^1$H-NMR: (DMSO, δ) 8.99 (d, J = 8.2 Hz, 1H), 8.80 (t, J = 5.6Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.62 - 7.34 (m, 7H), 5.05 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.80 (dd, J = 3.2 Hz, J = 14.4 Hz, 1H), 3.56 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-cyanobenzyl)ethyl]benzamide (Compound 69); Mass Spectrum: $(M+H^+)$ 411; $(M-H^+)$ 409; $^1$H NMR: (DMSO) 8.98 (d, J=8.2Hz, 1H), 8.81 (t, J=5.4Hz, 1H), 7.90- 7.46 (m, 9H), 5.05 (m, 1H), 4.68 (s, 2H), 4.14 (m, 2H), 3.82 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.58 (dd, , J=9.4Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-cyanobenzylsulfonyl)ethyl]benzamide (Compound 70); Mass Spectrum: $(M+H^+)$ 411; $(M-H^+)$ 409; $^1$H NMR: (DMSO) 8.98 (d, J=8.2Hz, 1H), 8.81 (t, J=5.4Hz, 1H), 7.91- 7.85 (m, 4H), 7.61-7.46 (m, 5H), 5.06

(m, 1H), 4.74 (s, 2H), 4.13 (m, 2H), 3.83 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.58 (dd, , J=9.4Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluoro-6-nitrobenzylsulfonyl)ethyl]benzamide (Compound 71); Mass Spectrum: $(M+H^+)$ 449; $(M-H^+)$ 447; : $^1$H NMR: (DMSO) 9.01 (d, J=8.2Hz, 1H), 8.87 (t, J=5.4Hz, 1H), 7.97-7.46 (m, 8H), 5.11-5.03 (m, 3H), 4.15 (m, 2H), 3.93 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.80 (dd, , J=9.7Hz, J=14.5Hz, 1H);

*N*-[2-(2-bromo-5-fluorobenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 72); Mass Spectrum: $(M+H^+)$ 482, 484; $(M-H^+)$ 480, 482; $^1$H-NMR: (DMSO, δ) 9.02 (d, J = 7.9 Hz, 1H), 8.85 (t, J = 5.4Hz, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.74 (dd, J = 5.4 Hz, J = 8.9 Hz, 1H) 7.60 - 7.46 (m, 3H), 7.40 (dd, J = 3.2 Hz, J = 10.8 Hz, 1H) 7.25 (dt, J = 3.2 Hz, J = 8.5 Hz, 1H) 5.10 (m, 1H), 4.77 (s, 2H), 4.15 (m, 2H), 3.88 (dd, J = 3.7 Hz, J = 14.4 Hz, 1H), 3.73 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,3-difluorobenzylsulfonyl)ethyl]benzamide (Compound 73); Mass Spectrum: $(M+H^+)$ 422; $(M-H^+)$ 420; $^1$H-NMR: (DMSO, δ) 9.00 (d, J = 8.2 Hz, 1H), 8.83 (t, J = 5.6Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.60 - 7.22 (m, 6H), 5.08 (m, 1H), 4.72 (s, 2H), 4.15 (m, 2H), 3.89 (dd, J = 3.0 Hz, J = 14.4 Hz, 1H), 3.70 (dd, J = 9.9 Hz, J = 14.4 Hz, 1H);

*N*-[2-biphenyl-2-ylmethylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 74); Mass Spectrum: $(M+H^+)$ 462; $(M-H^+)$ 460; $^1$H-NMR: (DMSO, δ) 8.90 (d, J = 8.4 Hz, 1H), 8.78 (t, J = 5.4Hz, 1H), 7.83 (d, J = 7.9 Hz, 2H), 7.60 - 7.28 (m, 12H), 4.93 (m, 1H), 4.51 (s, 2H), 4.11 (m, 2H), 3.61 (dd, J = 3.2 Hz, J = 14.4 Hz, 1H), 3.52 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl)-2-(2,4-difluorobenzylsulfonyl)ethyl]benzamide (Compound 75); Mass Spectrum: $(M+H^+)$ 422; $(M-H^+)$ 420; $^1$H NMR: (DMSO) 8.99 (d, J=8.2Hz, 1H), 8.83 (t, J=5.4Hz, 1H), 7.88 (m, 2H), 7.60-7.12 (m, 6H), 5.07 (m, 1H), 4.63 (s, 2H), 4.14 (m, 2H), 3.85 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.67 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-fluorobenzylsulfonyl)ethyl]benzamide (Compound 76); Mass Spectrum: $(M+H^+)$ 404; $(M-H^+)$ 402; $^1$H NMR: (DMSO) 8.98

(d, J=8.2Hz, 1H), 8.80 (t, J=5.4Hz, 1H), 7.88 (m, 2H), 7.60-7.40 (m, 5H), 7.23 (t, J=8.9Hz, 2H), 5.04 (m, 1H), 4.58 (s, 2H), 4.13 (m, 2H), 3.78 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.54 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1-*R*-cyanomethylcarbamoyl-2-(3,4-difluorobenzylsulfonyl)ethyl]benzamide (Compound 77); Mass Spectrum: $(M+H^+)$ 422; $(M-H^+)$ 420;

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,3,4-trifluorobenzylsulfonyl)ethyl]benzamide (Compound 78); Mass Spectrum: $(M+H^+)$ 440; $(M-H^+)$ 438;

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,4,6-trifluorobenzylsulfonyl)ethyl]benzamide (Compound 79); Mass Spectrum: $(M+H^+)$ 440; $(M-H^+)$ 438; $^1$H-NMR: (DMSO, δ) 9.01 (d, J = 8.2 Hz, 1H), 8.85 (t, J = 5.4Hz, 1H), 7.88 (d, J = 7.4 Hz, 2H), 7.60 - 7.46 (m, 3H), 7.31 (t, J = 8.7 Hz, 2H), 5.10 (m, 1H), 4.66 (s, 2H), 4.15 (m, 2H), 3.91 (dd, J = 2.5 Hz, J = 14.4 Hz, 1H), 3.76 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,4,5-trifluorobenzylsulfonyl)ethyl]benzamide (Compound 80); Mass Spectrum: $(M+H^+)$ 440; $(M-H^+)$ 438; $^1$H NMR: (DMSO) 8.98 (d, J=8.2Hz, 1H), 8.83 (t, J=5.4Hz, 1H), 7.88 (m, 2H), 7.71-7.46 (m, 5H), 5.07 (m, 1H), 4.64 (s, 2H), 4.14 (m, 2H), 3.87 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.69 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,3,6-trifluorobenzylsulfonyl)ethyl]benzamide (Compound 81); Mass Spectrum: $(M+H^+)$ 440; $(M-H^+)$ 438; $^1$H NMR: (DMSO) 9.01 (d, J=8.2Hz, 1H), 8.85 (t, J=5.4Hz, 1H), 7.88 (m, 2H), 7.66-7.46 (m, 4H), 7.29-7.20 (m, 1H), 5.11 (m, 1H), 4.76 (s, 2H), 4.15 (m, 2H), 3.96 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.78 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[2-(2-chloro-5-trifluoromethylbenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]-benzamide (Compound 82); Mass Spectrum: $(M+H^+)$ 487, 489; $(M-H^+)$ 485, 487; $^1$H-NMR: (DMSO, δ) 9.04 (d, J = 8.2 Hz, 1H), 8.86 (t, J = 5.4Hz, 1H), 7.92 - 7.87 (m, 3H), 7.79 (s, 2H), 7.60 - 7.44 (m, 3H), 5.11 (m, 1H), 4.92 (d, J = 13.6 Hz, 1H), 4.86 (d, J = 13.6 Hz, 1H), 4.15 (m, 2H), 3.92 (dd, J = 3.2 Hz, J = 14.6 Hz, 1H), 3.75 (dd, J = 9.9 Hz, J = 14.4 Hz, 1H);

*N*-[2-(2,4-bistrifluoromethylbenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]-benzamide (Compound 83); Mass Spectrum: $(M+H^+)$ 522; $(M-H^+)$ 520; $^1$H NMR: (DMSO) 9.04 (d, J=8.2Hz, 1H), 8.87 (t, J=5.4Hz, 1H), 8.17 (d, J=8.4Hz, 1H), 8.09 (s,

1H), 7.94-7.87 (m, 3H), 7.60-7.46 (m, 3H), 5.12 (m, 1H), 4.96 (d, J=14.3Hz, 1H), 4.88 (d, J=14.3Hz, 1H), 4.16 (m, 2H), 3.97 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.82 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluoro-6-trifluoromethylbenzylsulfonyl)ethyl]-benzamide (Compound 84); Mass Spectrum: $(M+H^+)$ 472; $(M-H^+)$ 470; $^1$H-NMR: (DMSO, δ) 9.01 (d, J = 8.4 Hz, 1H), 8.85 (t, J = 5.5Hz, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.70 - 7.45 (m, 6H), 5.08 (m, 1H), 4.80 (s, 2H), 4.13 (m, 2H), 3.97-3.75 (m, 2H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluoro-3-trifluoromethylbenzylsulfonyl)ethyl]-benzamide (Compound 85); Mass Spectrum: $(M+H^+)$ 472; $(M-H^+)$ 470; $^1$H NMR: (DMSO) 9.02 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.90-7.78 (m, 4H), 7.60-7.44 (m, 4H), 5.10 (m, 1H), 4.79 (s, 2H), 4.15 (m, 2H), 3.92 (dd, J=3.4Hz, J=14.3Hz, 1H), 3.72 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(3-trifluoromethylsulfanylbenzylsulfonyl)ethyl]-benzamide (Compound 86); Mass Spectrum: $(M+H^+)$ 486; $(M-H^+)$ 484; $^1$H-NMR: (DMSO, δ) 9.00 (d, J = 8.2 Hz, 1H), 8.80 (t, J = 5.4Hz, 1H), 7.90 - 7.46 (m, 9H), 5.05 (m, 1H), 4.70 (s, 2H), 4.13 (m, 2H), 3.82 (dd, J = 3.2 Hz, J = 14.9 Hz, 1H), 3.58 (dd, J = 9.7 Hz, J = 14.6 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluoro-4-trifluoromethylbenzylsulfonyl)ethyl]-benzamide (Compound 87); Mass Spectrum: $(M+H^+)$ 472; $(M-H^+)$ 470; $^1$H NMR: (DMSO) 9.00 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.90-7.46 (m, 8H), 5.10 (m, 1H), 4.78 (s, 2H), 4.15 (m, 2H), 3.92 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.71 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,3,5-trifluorobenzylsulfonyl)ethyl]benzamide (Compound 88); Mass Spectrum: $(M+H^+)$ 440; $(M-H^+)$ 438; $^1$H.NMR: (DMSO) 8.99 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.88 (m, 2H), 7.69-7.46 (m, 4H), 7.25-7.18 (m, 1H), 5.08 (m, 1H), 4.75 (s, 2H), 4.15 (m, 2H), 3.92 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.71 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-trifluoromethylsulfanylbenzylsulfonyl)ethyl]-benzamide (Compound 89); Mass Spectrum: $(M+H^+)$ 486; $(M-H^+)$ 484; $^1$H-NMR: (DMSO, δ) 9.04 (d, J = 8.2 Hz, 1H),

8.87 (t, J = 5.6Hz, 1H), 7.92 - 7.46 (m, 9H), 5.11 (m, 1H), 4.92 (s, 2H), 4.15 (m, 2H), 3.90 (dd, J = 3.5 Hz, J = 14.8 Hz, 1H), 3.77 (dd, J = 9.7 Hz, J = 14.6 Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(4-fluoro-2-trifluoromethylbenzylsulfonyl)ethyl]-benzamide (Compound 90); Mass Spectrum: $(M+H^+)$ 472; $(M-H^+)$ 470; $^1H$ NMR: (DMSO) 9.01 (d, J=8.2Hz, 1H), 8.86 (t, J=5.4Hz, 1H), 7.89 (m, 2H), 7.75-7.46 (m, 6H), 5.09 (m, 1H), 4.80 (d, J=14.3Hz, 1H), 4.73 (d, J=14.3Hz, 1H), 4.15 (m, 2H), 3.90 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.77 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluoro-5-trifluoromethylbenzylsulfonyl)ethyl]-benzamide (Compound 91); Mass Spectrum: $(M+H^+)$ 472; $(M-H^+)$ 470; $^1H$ NMR: (DMSO) 9.01 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.91-7.84 (m, 4H), 7.60-7.46 (m, 4H), 5.10 (m, 1H), 4.78 (s, 2H), 4.14 (m, 2H), 3.91 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.71 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-trifluoromethoxybenzylsulfonyl)ethyl]benzamide (Compound 92); Mass Spectrum: $(M+H^+)$ 470; $(M-H^+)$ 468; $^1H$-NMR: (DMSO, δ) 9.01 (d, J = 7.9 Hz, 1H), 8.84 (t, J = 5.3Hz, 1H), 7.89 (d, J = 7.7 Hz, 2H) 7.60 - 7.40 (m, 7H), 5.10 (m, 1H), 4.67 (s, 2H), 4.14 (m, 2H), 3.86 (dd, J = 3.2 Hz, J = 14.4 Hz, 1H), 3.70 (dd, J = 9.9 Hz, J = 14.4 Hz, 1H);

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[4-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-benzamide (Compound 93); Mass Spectrum: $(M+H^+)$ 452; $(M-H^+)$ 450; $^1H$ NMR: (DMSO) 8.99 (d, J=8.2Hz, 1H), 8.80 (t, J=5.4Hz, 1H), 7.88 (m, 2H), 7.60-7.42 (m, 5H), 7.27 (t, $J_{H,F}$=74Hz, 1H), 7.20 (d, J=8.4Hz, 2H), 5.05 (m, 1H), 4.58 (s, 2H), 4.14 (m, 2H), 3.79 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.55 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[2-(3,5-bistrifluoromethylbenzylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]-benzamide (Compound 94); Mass Spectrum: $(M+H^+)$ 522; $(M-H^+)$ 520; $^1H$ NMR: (DMSO) 9.00 (d, J=8.2Hz, 1H), 8.82 (t, J=5.6Hz, 1H), 8.17 (s, 1H), 8.13 (s, 2H), 7.88 (m, 2H), 7.60-7.46 (m, 3H), 5.07 (m, 1H), 4.89 (s, 2H), 4.14 (m, 2H), 3.88 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.63 (dd, , J=9.5Hz, J=14.5Hz, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-methoxybenzylsulfonyl)ethyl]benzamide

(Compound 95); Mass Spectrum: M + 1 = 416; NMR 270 MHz (DMSO): 8.3 (dd, 6, 1, 2H) 8 - 7.8 (m, 6H) 7.5 (d, 8, 1H) 7.4 (dd 8, 7, 1H) 5.6 (dd, 9, 3, 1H) 5.0 (d, 14, 1H) 4.6 (dd, 5,3, 2H) 4.8 (d 14, 1H) 4.6 (S, 2H) 4.2 (dd 15, 3, 1H) 3.8 (dd 15, 9, 1H);

*N*-[1*R*-cyanomethylcarbamoyl-2-(2,6-dichlorobenzylsulfonyl)ethyl]benzamide (Compound 96); Mass Spectrum: M + 1 = 454; NMR 270 MHz (acetone): 7.8 (d, 7, 2H) 7.4 (m, 6H) 5.3 (dd, 9, 3, 1H) 5.0 (d, 5, 2H) 4.2 (d, 3, 2H) 4.1 (dd 14, 3, 1H) 3.9 (dd, 14, 9, 1H);

*N*-(1*R*-cyanomethylcarbamoyl-3-pyrid-4-ylsulfonylpropyl)benzamide (Compound 97) MS: (M-1) = 385; NMR (1H): 8.95 (m, 2H), 8.72 (m, 2H), 7.88 (t, 2.2Hz, 2H), 7.78 (d, 1.7 Hz, 2H), 7.45-7.58 (m, 3H), 4.55 (m, 1H), 4.11 (d, 5.6 Hz, 2H), 3.51 (m, 2H), 2.10 (m, 2H);

*N*-(1*R*-cyanomethylcarbamoyl)-3-pyrid-2-ylsulfonylpropyl)benzamide (Compound 98) MS: (M-1) = 385; NMR: (1H): 8.6-8.77 (m, 2H), 8.18 (dt, 1.7, 7.6 Hz, 1H), 8.06 (d, 7.6 Hz, 1 H), 7.88 (d, 6.9 Hz, 2H), 7.72 (m, 1H), 7.45-7.58 (m, 4H), 4.12 (t, 2.7 Hz, 2H), 4.55 (m, 1H), 3.45-3.60 (m, 2H), 1.95-2.25 (m, 2H);

*N*-(1*R*-cyanomethylcarbamoyl-2-(3-difluoromethoxybenzylsulfonyl)ethyl]benzamide (Compound 99); Mass Spectrum: $(M+H^+)$ 452; $(M-H^+)$ 450; $^1$H-NMR: (DMSO, δ) 8.99 (d, J = 8.2 Hz, 1H), 8.81 (t, J = 6.2Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.60 - 7.18 (m, 7H), 7.22 (t, $J_{H,F}$ = 74 Hz, 1H), 5.05 (m, 1H), 4.62 (s, 2H), 4.14 (m, 2H), 3.81 (dd, J = 2.7 Hz, J = 14.5 Hz, 1H), 3.57 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H);

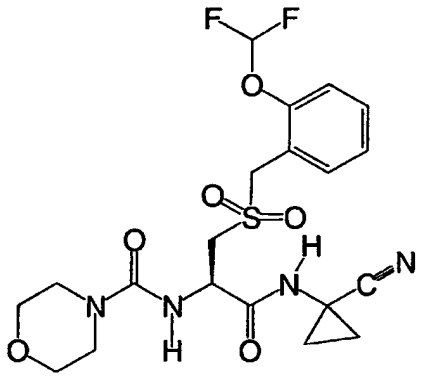
*N*-[1*R*-cyanomethylcarbamoyl-2-(4-fluoro-3-trifluoromethylbenzylsulfonyl)ethyl]-benzamide (Compound 100); Mass Spectrum: $(M+H^+)$ 472; $(M-H^+)$ 470; $^1$H NMR: (DMSO) 8.98 (d, J=8.2Hz, 1H), 8.81 (t, J=5.6Hz, 1H), 7.90-7.75 (m, 4H), 7.62-7.46 (m, 4H), 5.05 (m, 1H), 4.72 (s, 2H), 4.14 (m, 2H), 3.84 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.58 (dd, , J=9.5Hz, J=14.5Hz, 1H);

4-(2*R*-benzoylamino-2-cyanomethylcarbamoylethylsulfonylmethyl)benzoic acid (Compound 101); Mass Spectrum: $(M+H^+)$ 430; $(M-H^+)$ 428; $^1$H NMR: (DMSO) 8.98 (d, J=8.2Hz, 1H), 8.81 (t, J=5.6Hz, 1H), 7.95 (d, J=8.2Hz, 2H), 7.88 (m, 2H), 7.60-7.46 (m, 5H), 5.06 (m, 1H), 4.69 (s, 2H), 4.13 (m, 2H), 3.81 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.57 (dd, , J=9.5Hz, J=14.5Hz, 1H) and

*N*-[1*R*-(1-cyanocyclopropylcarbamoyl)-2-benzylsulfonylethyl]morpholine-4-carboxamide (Compound 103).

EXAMPLE 8

*N*-[1*R*-(1-cyanocyclopropylcarbamoyl)-2-(2-difluoromethoxybenzylsulfonyl)ethyl]-morpholine-4-carboxamide (Compound 104);

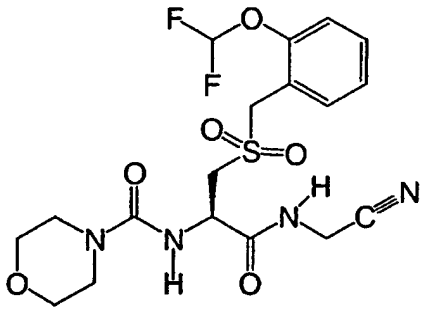


A mixture of (*R*)-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-[(1-morpholin-4-yl-methanoyl)-amino]-propionic acid (200 mg, 0.473 mmol), prepared as in Reference 7, in $CH_2Cl_2$ (3 mL), HATU (270 mg, 0.71 mmol) and HOAt (64.3 mg, 0.473 mmol) was treated with 1-amino-cyclopropanecarbonitrile (116 mg, 0.71 mmol) and N-methylmorpholine (0.156 mL, 1.42 mmol) and then DMF (3 mL) to obtain a homogenous solution. The mixture was stirred at room temperature for 16 hours, diluted with ethyl acetate (150 mL), washed with saturated aqueous $NaHCO_3$ and then brine, dried ($MgSO_4$) and concentrated to provide *N*-[1*R*-(1-cyanocyclopropylcarbamoyl)-2-(2-difluoromethoxybenzylsulfonyl)ethyl]-morpholine-4-carboxamide. The product was purified by flash chromatography. $^1$H NMR: (DMSO) 8.99 (s, 1H), 7.50-7.23 (m, 4H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 7.03 (d, J=8.4Hz, 1H), 4.64 (m, 1H), 4.55 (s, 2H), 3.64-3.24 (m, 10H), 1.47 (m, 2H), 1.14 (m, 2H).

EXAMPLE 9

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]morpholine-4-carboxamide

(Compound 102)

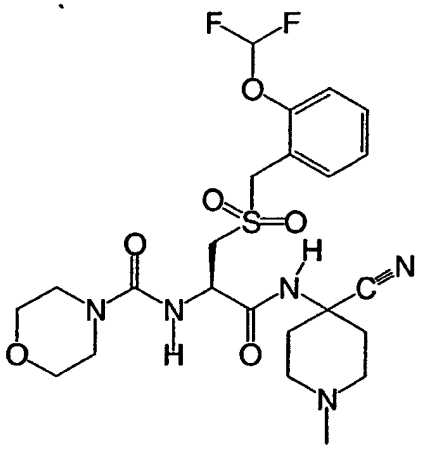


A solution of *N*-[2-*tert*-butyldisulfanyl-1*R*-cyanomethylcarbamoylethyl]morpholine-4-carboxamide (7.37 g, 20.4 mmol), provided as in Reference 8, in DMF (80 mL) was treated sequentially with tris(carboxyethyl)phosphine hydrochloride (7.03 g, 24.53 mmol) and aqueous potassium hydroxide solution (5N, 20 mL). The mixture was stirred for 5 hours and then treated with 2-difluoromethoxybenzyl bromide (14.54 g, 61.3 mmol). The mixture was stirred for 3 hours and then acidified with 1N hydrochloric acid. Product was extracted with ethyl acetate (3x150 mL) and the combined extracts were washed with brine, dried ($MgSO_4$) and concentrated. The residue was dissolved in methanol (500 mL) and then a saturated aqueous solution of Oxone® (200 mL) was added in one portion. The mixture was stirred for 2 hours and then concentrated under vacuum. Product was extracted from the residue with ethyl acetate (3x150 mL). The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated. Crude product was crystallized from ethyl acetate/hexane to provide *N*-[1*R*-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]morpholine-4-carboxamide (5.45 g) as a white crystalline solid. Mass Spectrum: $(M+H^+)$ 461; $(M-H^+)$ 459. $^1$H-NMR: (DMSO, δ) 8.69 (t, J = 5.4Hz, 1H), 7.54 - 7.09 (m, 4H), 7.14 (t, $J_{H,F}$ = 74 Hz, 1H), 4.73 (m, 1H), 4.56 (s, 2H), 4.13 (s, 2H), 3.68 - 3.25 (m, 10H).

EXAMPLE 10

Morpholine-4-carboxylic acid {(R)-1-(4-cyano-1-methyl-piperidin-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide

(Compound 121)



A solution of (*R*)-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-[(1-morpholin-4-yl-methanoyl)-amino]-propionic acid (200 mg, 0.473 mmol), provided as in Reference 1, in $CH_2Cl_2$ (3 mL) was combined with HATU (270 mg, 0.71 mmol), HOAt (64.3 mg, 0.473 mmol), 4-amino-1-methyl-piperidine-4-carbonitrile (98 mg, 0.71 mmol), N-methylmorpholine (0.156 mL, 1.42 mmol) and then DMF (3 mL) to obtain a homogenous solution. The mixture was stirred at room temperature for 16 hours, diluted with ethyl acetate (150 mL), washed with saturated aqueous $NaHCO_3$ and then brine, dried ($MgSO_4$) and concentrated. The product was purified from the residue by flash chromatography to provide morpholine-4-carboxylic acid {(*R*)-1-(4-cyano-1-methyl-piperidin-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide. $^1$H NMR: (DMSO) 8.62 (s, 1H), 7.51-7.23 (m, 4H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 7.06 (d, J=8.6Hz, 1H), 4.70 (m, 1H), 4.57 (s, 2H), 3.57-3.25 (m, 10H), 2.62-1.82 (m, 11H).

The following compounds of Formula I are provided by the methods described

in this Application:

*N*-[1*R*-cyanomethylcarbamoyl-2-(3,5-dimethylisoxazol-4-ylmethylsulfonyl)ethyl]-benzamide (Compound 105); $^1$H NMR: (DMSO) 9.02 (d, J=8.4Hz, 1H), 8.83 (t, J=5.6Hz, 1H), 7.89 (m, 2H), 7.60-7.46 (m, 3H), 5.10 (m, 1H), 4.51 (d, J=14.5Hz, 1H), 4.41 (d, J=14.5Hz, 1H), 4.15 (m, 2H), 3.89 (dd, J=3.4Hz, J=14.5Hz, 1H), 3.66 (dd, , J=9.5Hz, J=14.5Hz, 1H), 2.37 (s, 3H), 2.18 (s, 3H). MS: ($M^+$+1) 430;

*N*-[2-(5-chlorothien-2-ylmethylsulfonyl)-1*R*-cyanomethylcarbamoylethyl]benzamide (Compound 106); $^1$H NMR: (DMSO) 9.00 (d, J=8.2Hz, 1H), 8.80 (t, J=5.6Hz, 1H), 7.88 (m, 2H), 7.60-7.46 (m, 3H), 7.09 (d, J=3.7Hz, 1H), 7.04 (d, J=3.7Hz, 1H), 5.03 (m, 1H), 4.87 (d, J=14.7Hz, 1H), 4.80 (d, J=14.7Hz, 1H), 4.13 (m, 2H), 3.84 (dd, J=3.2Hz, J=14.3Hz, 1H), 3.59 (dd, , J=9.5Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 426;

*N*-[1*R*-cyanomethylcarbamoyl-2-(2-fluoro-3-methylbenzylsulfonyl)ethyl]benzamide (Compound 107); Mass Spectrum: ($M+H^+$) 418; ($M-H^+$) 416; $^1$H-NMR: (DMSO, δ) 8.99 (d, J = 7.9 Hz, 1H), 8.82 (t, J = 5.7Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.60 - 7.45 (m, 3H), 7.34 - 7.25 (m, 2H), 7.12 (t, J = 7.5 Hz, 1H), 5.07 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.86 (dd, J = 3.2 Hz, J = 14.4 Hz, 1H), 3.66 (dd, J = 9.7 Hz, J = 14.4 Hz, 1H), 2.23 (s, 3H);

*N*-[1-(Cyanomethyl-carbamoyl)-2-(1-oxy-pyridin-2-ylmethanesulfonyl)-ethyl]-benzamide (Compound 108) Mass Spec: MW = 402.4, (M+1) = 403.0;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-1-oxy-nicotinamide (Compound 109); $^1$H NMR: (DMSO) 9.32 (d, J=8.2Hz, 1H), 8.91 (t, J=5.6Hz, 1H), 8.62 (s, 1H), 8.39 (d, J=6.4Hz, 1H), 7.70 (d, J=8.2Hz, 1H), 7.58-7.44 (m, 3H), 7.32-7.24 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 5.05 (m, 1H), 4.62 (s, 2H), 4.16 (m, 2H), 3.83 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.58 (dd, , J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 469;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-nicotinamide (Compound 110); $^1$H NMR: (DMSO) 9.21 (d, J=7.9 Hz, 1H), 9.03 (s, 1H), 8.88 (t, J=5.4Hz, 1H), 8.73 (dd, J=1.5Hz, J=4.7Hz,

1H), 8.20 (m, 1H), 7.57-7.44 (m, 3H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.10 (m, 1H), 4.62 (s, 2H), 4.15 (m, 2H), 3.84 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.62 (dd, , J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 453;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-isonicotinamide (Compound 111); $^1$H NMR: (DMSO) 9.31 (d, J=8.4 Hz, 1H), 8.90 (t, J=5.4Hz, 1H), 8.77-8.75 (m, 2H), 8.78-8.76 (m, 2H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 5.09 (m, 1H), 4.62 (s, 2H), 4.15 (m, 2H), 3.83 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.63 (dd, , J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 453;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-1-oxy-isonicotinamide (Compound 112); $^1$H NMR: (DMSO) 9.25 (d, J=8.2 Hz, 1H), 8.90 (t, J=5.4Hz, 1H), 8.35 (d, J=7.2Hz, 2H), 7.82 (d, J=7.2Hz, 2H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.05 (m, 1H), 4.61 (s, 2H), 4.15 (m, 2H), 3.82 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.60 (dd, , J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 469;

Pyridine-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 113); $^1$H NMR: (DMSO) 9.34 (d, J=8.8 Hz, 1H), 8.78 (t, J=5.4Hz, 1H), 8.68 (d, J=4.7Hz, 1H), 8.09-7.99 (m, 2H), 7.64 (t, J=6.2Hz, 1H), 7.49-7.43 (m, 2H), 7.30-7.22 (m, 2H), 7.10 (t, $J_{H,F}$=74Hz, 1H), 5.13 (m, 1H), 4.58 (s, 2H), 4.12 (m, 2H), 3.93-3.77 (m, 2H). MS: ($M^+$+1) 453;

Pyrazine-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 114); $^1$H NMR: (DMSO) 9.46 (d, J=8.7 Hz, 1H), 9.22 (d, J=1.5Hz, 1H), 8.91 (d, J=2.5Hz, 1H), 8.82-8.77 (m, 2H), 7.51-7.43 (m, 2H), 7.31-7.21 (m, 2H), 7.11 (t, $J_{H,F}$=74Hz, 1H), 5.16 (m, 1H), 4.58 (s, 2H), 4.13 (m, 2H), 3.91-3.78 (m, 2H). MS: ($M^+$+1) 454;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-2-hydroxy-nicotinamide (Compound 115); $^1$H NMR: (DMSO) 10.38 (d, J=7.8Hz, 1H), 8.88 (t, J=5.4Hz, 1H), 8.32 (dd, J=1.5Hz, J=7.2Hz, 1H), 7.74 (m, 1H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.11 (t, $J_{H,F}$=74Hz, 1H), 6.49 (t, J=6.6Hz, 1H), 5.07 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.73 (d, J=6.4Hz, 2H). MS: ($M^+$+1) 469;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-6-hydroxy-nicotinamide (Compound 116); $^1$H NMR: (DMSO) 12.03 (s, 1H), 8.83-8.77 (m, 2H), 8.01 (d, J=2.2Hz, 1H), 7.84 (dd, J=2.5Hz, J=9.4Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 6.38 (d, J=9.6Hz, 1H), 4.99 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.78 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.55 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 469;

2-Amino-*N*-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenyl-methanesulfonyl]-ethyl}-nicotinamide (Compound 117); $^1$H NMR: (DMSO) 8.91 (d, J=7.9Hz, 1H), 8.82 (t, J=5.4Hz, 1H), 8.10 (d, J=3.7Hz, 1H), 7.94 (d, J=7.7Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 7.05 (s, 2H), 6.61 (dd, J=4.7Hz, J=7.4Hz, 1H), 5.03 (m, 1H), 4.60 (s, 2H), 4.13 (m, 2H), 3.80 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.62 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 468;

6-Amino-*N*-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide (Compound 118); $^1$H NMR: (DMSO) 8.76 (t, J=5.4Hz, 1H), 8.66 (d, J=8.4Hz, 1H), 8.48 (s, 1H), 7.81 (d, J=8.5Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 6.56 (s, 2H), 6.43 (d, J=8.7Hz, 1H), 5.02 (m, 1H), 4.58 (s, 2H), 4.12 (m, 2H), 3.77 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.61 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 468;

3-Hydroxy-pyridine-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 119); $^1$H NMR: (DMSO) 12.04 (s, 1H), 9.64 (d, J=9.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 8.20 (d, J=4.5Hz, 1H), 7.57 (dd, J=4.5Hz, J=8.7Hz, 1H), 7.52-7.44 (m, 3H), 7.31-7.22 (m, 2H), 7.11 (t, $J_{H,F}$=74Hz, 1H), 5.15 (m, 1H), 4.60 (s, 2H), 4.14 (m, 2H), 3.94-3.81 (m, 2H). MS: ($M^+$+1) 469;

Morpholine-4-carboxylic acid {(R)-1-(4-cyano-tetrahydro-pyran-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 120); $^1$H NMR: (DMSO) 8.75 (s, 1H), 7.51-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 7.04 (d, J=8.4Hz, 1H), 4.72 (m, 1H), 4.57 (s, 2H), 3.78 (m, 2H), 3.60-3.25 (m, 12H), 2.24-2.10 (m, 2H), 1.98-1.84 (m, 2H). MS: ($M^+$+1) 531;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(3-pyridin-3-yl-ureido)-propionamide (Compound 122); $^1$H NMR: (DMSO) 9.08 (s, 1H),

8.90 (t, J=5.4Hz, 1H), 8.55 (d, J=2.5Hz, 1H), 8.14 (dd, J=1.2Hz, J=4.7Hz, 1H), 7.90 (m, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 3H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 6.84 (d, J=8.9Hz, 1H), 4.84 (m, 1H), 4.61 (s, 2H), 4.15 (m, 2H), 3.70 (dd, J=4.2Hz, J=14.5Hz, 1H), 3.60 (dd, J=8.4Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 468;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(3-pyridin-4-yl-ureido)-propionamide (Compound 123); $^1$H NMR: (DMSO) 9.34 (s, 1H), 8.92 (t, J=5.4Hz, 1H), 8.31 (d, J=5.9Hz, 2H), 7.52-7.37 (m, 4H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 6.92 (d, J=8.4Hz, 1H), 4.84 (m, 1H), 4.61 (s, 2H), 4.15 (m, 2H), 3.71 (dd, J=4.2Hz, J=14.5Hz, 1H), 3.61 (dd, J=8.4Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 468;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(3-isopropyl-ureido)-propionamide (Compound 124); $^1$H NMR: (DMSO) 8.76 (t, J=5.4Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 6.31 (d, J=8.7Hz, 1H), 6.15 (d, J=7.7Hz, 1H), 4.71 (m, 1H), 4.55 (s, 2H), 4.12 (m, 2H), 3.75-3.40 (m, 3H), 1.03 (d, J=6.4Hz, 6H). MS: ($M^+$+1) 433;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(3,3-dimethyl-ureido)-propionamide (Compound 125); $^1$H NMR: (DMSO) 8.65 (t, J=5.4Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 6.84 (d, J=7.0Hz, 1H), 4.71 (m, 1H), 4.55 (s, 2H), 4.11 (m, 2H), 3.68-3.51 (m, 2H), 2.82 (s, 6H). MS: ($M^+$+1) 419;

(R)-2-Acetylamino-*N*-cyanomethyl-3-phenylmethanesulfonyl-propionamide (Compound 126);

*N*-[(R)-1-(Cyanomethyl-carbamoyl)-2-phenylmethanesulfonyl-ethyl]-2-methoxy-benzamide (Compound 127);

*N*-[(S)-1-(Cyanomethyl-carbamoyl)-3-phenylmethanesulfonyl-propyl]-benzamide (Compound 128); $^1$H NMR: (DMSO) 8.7 (m, 2H), 7.91 (d, J=7Hz, 2H), 7.5 (m, 3H), 7.35 (m, 5H), 4.56 (m, 1H), 4.51 (s, 2H), 4.15 (d, J=6Hz, 2H), 3.1 (m, 2H), 2.2 (m, 2H). MS: (m/e) = 400.2;

Morpholine-4-carboxylic acid {(R)-1-[(1,1-dicyano-methyl)-carbamoyl]-2-phenyl-methanesulfonyl-ethyl}-amide (Compound 129);

2-(2-Benzenesulfonyl-ethyl)-*N*-benzyl-*N*'-cyanomethyl-malonamide

(Compound 130); $^1$H NMR: (DMSO) 8.57 (t, J=6Hz, 1H), 8.43 (t, J=6Hz, 1H), 7.86 (d, J=7Hz, 2H), 7.79 (t, J=5Hz, 1H), 7.68 (t, J=8Hz, 2H), 7.15 (m, 5H), 4.26 (d, J=6Hz, 2H), 4.13 (d, J=6Hz, 2H), 3.35 (m, 1H), 3.19 (m, 2H), 2.00 (m, 2H). MS: (M/e) = 400.04;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid methyl ester (Compound 131); $^1$H NMR: (DMSO) 8.87 (t, J=5.4Hz, 1H), 7.75 (d, J=8.6Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 4.62 (m, 1H), 4.57 (s, 2H), 4.12 (m, 2H), 3.66 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.57 (s, 3H), 3.42 (dd, J=9.4Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 406;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid allyl ester (Compound 132); $^1$H NMR: (DMSO) 8.87 (t, J=5.4Hz, 1H), 7.84 (d, J=8.6Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 5.90 (m, 1H), 5.31 (d, J=17Hz, 1H), 5.18 (d, J=10.6Hz, 1H), 4.62 (m, 1H), 4.57 (s, 2H), 4.51 (m, 2H), 4.12 (m, 2H), 3.66 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.44 (dd, J=9.4Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 432;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid isopropyl ester (Compound 133); $^1$H NMR: (DMSO) 8.80 (t, J=5.4Hz, 1H), 7.60 (d, J=8.4Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 4.77 (sept, J=6.4Hz, 1H), 4.62 (m, 1H), 4.56 (s, 2H), 4.13 (m, 2H), 3.64 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.43 (dd, J=9.4Hz, J=14.5Hz, 1H), 1.19 (d, J=6.4Hz, 3H), 1.16 (d, J=6.4Hz, 3H). MS: ($M^+$+1) 434;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid isobutyl ester (Compound 134); $^1$H NMR: (DMSO) 8.82 (t, J=5.4Hz, 1H), 7.71 (d, J=8.7Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 4.61 (m, 1H), 4.56 (s, 2H), 4.13 (m, 2H), 3.86-3.69 (m, 2H), 3.65 (dd, J=3.4Hz, J=14.5Hz, 1H), 3.44 (dd, J=9.6Hz, J=14.5Hz, 1H), 1.84 (sept, J=6.4Hz, 1H), 0.88 (d, J=6.6Hz, 6H). MS: ($M^+$+1) 448;

(R)-*N*-Cyanomethyl-2-(1-oxo-1,3-dihydro-isoindol-2-yl)-3-phenylmethanesulfonyl-propionamide (Compound 135); $^1$H NMR: (DMSO) 8.93 (t, J=5.4Hz, 1H), 7.72 (d, J=7.7Hz, 1H), 7.64-7.36 (m, 8H), 5.32 (m, 1H), 4.65-5.52 (m, 3H), 4.43 (d, J=17Hz, 1H), 4.12 (m, 2H), 3.92-3.77 (m, 2H). MS: ($M^+$+1) 398;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3,4-difluoro-benzamide (Compound 136); $^1$H NMR: (DMSO) 9.12 (d, J=8.2Hz, 1H), 8.87 (t, J=5.4Hz, 1H), 7.90 (m, 1H), 7.76 (m, 1H), 7.65-7.44 (m, 3H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.06 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.82 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.61 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 488;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3,4-dimethoxy-benzamide (Compound 137); $^1$H NMR: (DMSO) 8.86 (d, J=8.2Hz, 1H), 8.80 (t, J=5.4Hz, 1H), 7.54-7.44 (m, 4H), 7.32-7.23 (m, 2H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 7.05 (d, J=8.4Hz, 1H), 5.05 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.64 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 512;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-methyl-benzamide (Compound 138); $^1$H NMR: (DMSO) 8.94 (d, J=8.2Hz, 1H), 8.80 (t, J=5.4Hz, 1H), 7.71-7.64 (m, 2H), 7.52-7.23 (m, 6H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.07 (m, 1H), 4.60 (s, 2H), 4.13 (m, 2H), 3.81 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.65 (dd, J=10.0Hz, J=14.5Hz, 1H), 2.37 (s, 3H). MS: ($M^+$+1) 466;

Thiophene-3-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 139); $^1$H NMR: (DMSO) 8.86 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 8.18 (dd, J=1.0Hz, J=2.7Hz, 1H), 7.61 (dd, J=2.9Hz, J=4.9Hz, 1H), 7.53-7.44 (m, 3H), 7.32-7.23 (m, 2H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 5.02 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.79 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.60 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 458;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-4-fluoro-benzamide (Compound 140); $^1$H NMR: (DMSO) 9.03 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.97-7.92 (m, 2H), 7.53-7.23 (m, 6H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.07 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.81 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.64 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 470;

4-Methyl-pentanoic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 141); $^1$H NMR: (DMSO)

8.73 (t, J=5.4Hz, 1H), 8.41 (d, J=8.4Hz, 1H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 4.83 (m, 1H), 4.56 (s, 2H), 4.12 (m, 2H), 3.67 (dd, J=3.9Hz, J=14.5Hz, 1H), 3.39 (dd, J=9.0Hz, J=14.5Hz, 1H), 2.14 (t, J=7.4Hz, 2H), 1.58-1.35 (m, 3H), 0.84 (d, J=6.4Hz, 6H). MS: ($M^+$+1) 446;

Thiophene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 142); $^1$H NMR: (DMSO) 9.02 (d, J=8.2Hz, 1H), 8.87 (t, J=5.4Hz, 1H), 7.80 (m, 2H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.18 (dd, J=3.9Hz, J=4.9Hz, 1H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 5.02 (m, 1H), 4.60 (s, 2H), 4.14 (m, 2H), 3.80 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.61 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 458;

4-Bromo-*N*-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenyl-methanesulfonyl]-ethyl}-benzamide (Compound 143); $^1$H NMR: (DMSO) 9.08 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.82 (d, J=8.7Hz, 2H), 7.72 (d, J=8.7Hz, 2H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.06 (m, 1H), 4.60 (s, 2H), 4.14 (m, 2H), 3.81 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.62 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 530, 532;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-4-methoxy-benzamide (Compound 144); $^1$H NMR: (DMSO) 8.83 (d, J=8.2Hz, 1H), 8.78 (t, J=5.4Hz, 1H), 7.86 (d, J=8.6Hz, 2H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 7.02 (d, J=8.7Hz, 2H), 5.05 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.81 (s, 3H), 3.79 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.64 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 482;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-4-trifluoromethoxy-benzamide (Compound 145); $^1$H NMR: (DMSO) 9.12 (d, J=8.2Hz, 1H), 8.85 (t, J=5.4Hz, 1H), 8.00 (d, J=8.6Hz, 2H), 7.54-7.44 (m, 4H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.08 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.82 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.63 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 536;

Naphthalene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 146); $^1$H NMR: (DMSO) 9.18 (d, J=8.2Hz, 1H), 8.87 (t, J=5.4Hz, 1H), 8.49 (s, 1H), 8.05-7.94 (m, 4H),

7.66-7.57 (m, 2H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.14 (m, 1H), 4.63 (s, 2H), 4.16 (m, 2H), 3.85 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.69 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 502;

(E)-*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-phenyl-acrylamide (Compound 147); $^1$H NMR: (DMSO) 8.88 (t, J=5.4Hz, 1H), 8.78 (d, J=8.2Hz, 1H), 7.61-7.38 (m, 8H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 6.66 (d, J=16Hz, 1H), 4.99 (m, 1H), 4.60 (s, 2H), 4.14 (m, 2H), 3.75 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.49 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 478;

5-Methyl-thiophene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 148); $^1$H NMR: (DMSO) 8.87 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.59 (d, J=3.7Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 6.86 (m, 1H), 4.99 (m, 1H), 4.58 (s, 2H), 4.13 (m, 2H), 3.78 (dd, J=3.4Hz, J=14.5Hz, 1H), 3.63 (dd, J=10.0Hz, J=14.5Hz, 1H), 2.47 (s, 3H). MS: ($M^+$+1) 472;

Biphenyl-4-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 149); $^1$H NMR: (DMSO) 9.06 (d, J=8.4Hz, 1H), 8.86 (t, J=5.4Hz, 1H), 7.98 (d, J=8.4Hz, 2H), 7.81 (d, J=8.4Hz, 2H), 7.74 (d, J=7.4Hz, 2H), 7.53-7.38 (m, 5H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 5.11 (m, 1H), 4.61 (s, 2H), 4.15 (m, 2H), 3.83 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.68 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 528;

1*H*-Indole-5-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide; (Compound 150); $^1$H NMR: (DMSO) 11.36 (s, 1H), 8.83 (d, J=8.2Hz, 1H), 8.78 (t, J=5.4Hz, 1H), 8.18 (s, 1H), 7.66 (dd, J=1.7Hz, J=8.4Hz, 1H), 7.53-7.42 (m, 4H), 7.32-7.23 (m, 2H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 6.55 (m, 1H), 5.10 (m, 1H), 4.60 (s, 2H), 4.14 (m, 2H), 3.80 (dd, J=3.5Hz, J=14.5Hz, 1H), 3.70 (dd, J=9.2Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 491;

Benzo[1,3]dioxole-5-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 151); $^1$H NMR: (DMSO) 8.83 (d, J=8.2Hz, 1H), 8.79 (t, J=5.4Hz, 1H), 7.52-7.39 (m, 4H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 7.02 (d, J=8.2Hz, 1H), 6.10 (s, 2H), 5.03 (m,

1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.78 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.62 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 496;

Benzo[*b*]thiophene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 152); $^1$H NMR: (DMSO) 9.30 (d, J=8.2Hz, 1H), 8.92 (t, J=5.4Hz, 1H), 8.12 (s, 1H), 8.06-7.97 (m, 2H), 7.53-7.40 (m, 4H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.07 (m, 1H), 4.62 (s, 2H), 4.16 (m, 2H), 3.83 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.63 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 508;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-phenoxy-benzamide (Compound 153); $^1$H NMR: (DMSO) 9.04 (d, J=8.2Hz, 1H), 8.82 (t, J=5.4Hz, 1H), 7.66 (d, J=8.2Hz, 1H), 7.55-7.37 (m, 6H), 7.32-7.14 (m, 4H), 7.12 (t, $J_{H,F}$=74Hz, 1H), 7.03 (d, J=7.7Hz, 2H), 5.05 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.79 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.63 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 544;

Quinoline-3-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 154); $^1$H NMR: (DMSO) 9.40 (d, J=8.2Hz, 1H), 9.30 (d, J=2.2Hz, 1H), 8.95 (t, J=5.4Hz, 1H), 8.84 (d, J=2.0Hz, 1H), 8.12 (dd, J=3.7Hz, J=7.9Hz, 2H), 7.89 (t, J=7.4Hz, 1H), 7.71 (t, J=7.7Hz, 1H), 7.54-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 5.17 (m, 1H), 4.65 (s, 2H), 4.17 (m, 2H), 3.88 (dd, J=3.0Hz, J=14.5Hz, 1H), 3.63 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 503;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-(1-phenyl-methanoyl)-benzamide (Compound 155); $^1$H NMR: (DMSO) 9.22 (d, J=8.2Hz, 1H), 8.87 (t, J=5.4Hz, 1H), 8.27 (s, 1H), 8.17 (d, J=7.9Hz, 1H), 7.90 (d, J=7.9Hz, 1H), 7.78-7.66 (m, 4H), 7.59-7.44 (m, 4H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.09 (m, 1H), 4.61 (s, 2H), 4.14 (m, 2H), 3.82 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.65 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 556;

4-Chloro-*N*-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenyl-methanesulfonyl]-ethyl}-benzamide (Compound 156); $^1$H NMR: (DMSO) 9.08 (d, J=8.2Hz, 1H), 8.84 (t, J=5.4Hz, 1H), 7.89 (d, J=8.4Hz, 2H), 7.58 (d, J=8.4Hz, 2H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.07 (m, 1H), 4.60 (s,

2H), 4.14 (m, 2H), 3.81 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.63 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 486, 488;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-fluoro-4-methoxy-benzamide (Compound 157); $^1$H NMR: (DMSO) 8.94 (d, J=8.2Hz, 1H), 8.83 (t, J=5.4Hz, 1H), 7.75-7.68 (m, 2H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 3H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.05 (m, 1H), 4.59 (s, 2H), 4.13 (m, 2H), 3.90 (s, 3H), 3.80 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.62 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 500;

3-Bromo-thiophene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 158); $^1$H NMR: (DMSO) 8.89 (t, J=5.4Hz, 1H), 8.59 (d, J=8.2Hz, 1H), 7.86 (d, J=5.2Hz, 1H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.21 (d, J=5.2Hz, 1H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.04 (m, 1H), 4.61 (s, 2H), 4.16 (m, 2H), 3.79 (dd, J=3.5Hz, J=14.5Hz, 1H), 3.70 (dd, J=9.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 536, 538;

3-Chloro-benzo[*b*]thiophene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 159); $^1$H NMR: (DMSO) 8.96 (t, J=5.4Hz, 1H), 8.82 (d, J=8.2Hz, 1H), 8.17-8.10 (m, 1H), 7.96-7.89 (m, 1H), 7.64-7.56 (m, 2H), 7.54-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 5.14 (m, 1H), 4.64 (s, 2H), 4.19 (m, 2H), 3.88-3.73 (m, 2H). MS: ($M^+$+1) 542, 544;

3-Chloro-thiophene-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 160); $^1$H NMR: (DMSO) 8.88 (t, J=5.4Hz, 1H), 8.49 (d, J=8.2Hz, 1H), 7.90 (d, J=5.4Hz, 1H), 7.52-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.18 (d, J=5.4Hz, 1H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.05 (m, 1H), 4.61 (s, 2H), 4.16 (m, 2H), 3.82-3.70 (m, 2H). MS: ($M^+$+1) 492, 494;

*N*-{(R)-(Cyanomethyl-carbamoyl)-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-trifluoromethyl-benzamide (Compound 161); $^1$H NMR: (DMSO) 9.24 (d, J=8.2Hz, 1H), 8.88 (t, J=5.4Hz, 1H), 8.07 (d, J=8.2Hz, 2H), 7.90 (d, J=8.4Hz, 2H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.13 (t, $J_{H,F}$=74Hz, 1H), 5.11 (m, 1H), 4.62 (s, 2H), 4.15 (m, 2H), 3.83 (dd, J=3.2Hz, J=14.5Hz, 1H), 3.64 (dd, J=10.0Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 520;

Quinoline-2-carboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 162); $^1$H NMR: (DMSO) 9.51 (d, J=8.2Hz, 1H), 8.85 (t, J=5.4Hz, 1H), 8.60 (d, J=8.4Hz, 1H), 8.20 (d, J=8.4Hz, 1H), 8.16-8.08 (m, 2H), 7.89 (t, J=7.0Hz, 1H), 7.74 (t, J=7.0Hz, 1H), 7.53-7.44 (m, 2H), 7.32-7.23 (m, 2H), 7.11 (t, $J_{H,F}$=74Hz, 1H), 5.21 (m, 1H), 4.62 (s, 2H), 4.14 (m, 2H), 4.00-3.82 (m, 2H). MS: ($M^+$+1) 503;

(R)-2-Benzenesulfonylamino-*N*-cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-propionamide (Compound 163); $^1$H NMR: (DMSO) 9.02 (t, J=5.4Hz, 1H), 8.57 (d, J=9.2Hz, 1H), 8.77 (m, 2H), 7.65-7.23 (m, 7H), 7.11 (t, $J_{H,F}$=74Hz, 1H), 4.52 (d, J=13.6Hz, 1H), 4.44 (d, J=13.6Hz, 1H), 4.38 (m, 1H), 4.01-3.85 (m, 2H), 3.47 (dd, J=5.9Hz, J=14.5Hz, 1H), 3.22 (dd, J=7.2Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 488;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(naphthalene-2-sulfonylamino)-propionamide (Compound 164); $^1$H NMR: (DMSO) 9.05 (t, J=5.4Hz, 1H), 8.67 (d, J=9.0Hz, 1H), 8.43 (s, 1H), 8.14-8.01 (m, 3H), 7.78 (dd, J=2.0Hz, J=8.6Hz, 1H), 7.74-6.63 (m, 2H), 7.46-7.39 (m, 1H), 7.27-7.14 (m, 3H), 7.07 (t, $J_{H,F}$=74Hz, 1H), 4.52-4.37 (m, 3H), 3.86 (m, 2H), 3.49 (dd, J=5.7Hz, J=14.5Hz, 1H), 3.26 (dd, J=7.2Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 538;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(thiophene-2-sulfonylamino)-propionamide (Compound 165); $^1$H NMR: (DMSO) 9.06 (t, J=5.4Hz, 1H), 8.78 (d, J=9.1Hz, 1H), 7.91 (d, J=4.9Hz, 1H), 7.57 (d, J=3Hz, 1H), 7.51-7.40 (m, 2H), 7.32-7.23 (m, 2H), 7.12 (m, 1H), 7.11 (t, $J_{H,F}$=74Hz, 1H), 4.54 (d, J=13.8Hz, 1H), 4.47 (d, J=13.8Hz, 1H), 4.42 (m, 1H), 4.10-3.95 (m, 2H), 3.50 (dd, J=5.9Hz, J=14.5Hz, 1H), 3.24 (dd, J=7.2Hz, J=14.5Hz, 1H). MS: ($M^+$+1) 494;

Cyclopentanecarboxylic acid {(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide (Compound 166); $^1$H NMR: (DMSO) 8.69 (t, J=5.4Hz, 1H), 8.34 (d, J=8.4Hz, 1H), 7.52-7.44 (m, 2H), 7.33-7.23 (m, 2H), 7.14 (t, $J_{H,F}$=74Hz, 1H), 4.84 (m, 1H), 4.56 (s, 2H), 4.12 (m, 2H), 3.67 (dd, J=3.9Hz, J=14.5Hz, 1H), 3.41 (dd, J=9.2Hz, J=14.5Hz, 1H), 2.62 (m, 1H), 1.76-1.45 (m, 8H). MS: ($M^+$+1) 444;

Morpholine-4-carboxylic acid {(R)-1-[(1-cyano-1-thiophen-2-yl-methyl)-

carbamoyl]-2-phenylmethanesulfonyl-ethyl}-amide (Compound 172); $^1$H-NMR (CdCl3) delta (ppm): 8.17 (m, 1H), 7.40 (m, 5H), 7.35 (t, J=1.0 Hz, 1H), 7.28, 7.26 (t, J=1.0 Hz, 1H), 7.02-7.00 (d, J=3.5 Hz, 1H), 6.17 (d, J=7.9 Hz, 1H), 5.98 (m, 1H), 4.90 (m, 1H), 4.50 (dd, J=8.9, 9.1 Hz, 1H), 4.35 (dd, J=6.2, 5.7 Hz, 1H), 3.65 (m, 5H), 3.20-3.40 (m, 5H); MS M+=476.8 M-=474.8; and

Morpholine-4-carboxylic acid {(R)-1-[(1-cyano-1-furan-2-yl-methyl)-carbamoyl]-2-phenylmethanesulfonyl-ethyl}-amide (Compound 174) $^1$H NMR (DMSO, 300 MHz) 9.9 and 9.36 pair of diastereomers (pair of doublets, J = 3.5 Hz, 1H), 7.37 (m, 5H), 7.08 (m, 1H), 7.36 (t, 3.5 Hz, 1H), 6.16 (d, 7.4 Hz, 1H), 6.11 (m, 1H), 4.72, (m, 1H), 4.49 (d, 5.9 Hz, 2 H), 3.2-3.7 (m, 10 H), 2.26 (s, 3H); MS (M-1) = 472.8.

## EXAMPLE 11

### Cathepsin S Assay

Solutions of test compounds in varying concentrations were prepared in 10 µL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 µL, comprising: MES, 50 mM (pH 6.5); EDTA, 2.5 mM; and NaCl, 100 mM). Human cathepsin S (0.158 pMoles in 25 µL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-Val-Val-Arg-AMC (9 nMoles in 25 µL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at ($\lambda$ 460 nm) for 5 minutes. Apparent inhibition constants ($K_i$) were calculated from the enzyme progress curves using standard mathematical models.

## EXAMPLE 12

### Cathepsin B Assay

Solutions of test compounds in varying concentrations were prepared in 10 µL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 µL, comprising: *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), 50 mM (pH 6);

polyoxyethylenesorbitan monolaurate, 0.05%; and dithiothreitol (DTT), 2.5 mM). Human cathepsin B (0.025 pMoles in 25 µL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-FR-AMC (20 nMoles in 25 µL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at (λ 460 nm) for 5 minutes. Apparent inhibition constants ($K_i$) were calculated from the enzyme progress curves using standard mathematical models.

## EXAMPLE 13

## Cathepsin K Assay

Solutions of test compounds in varying concentrations were prepared in 10 µL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 µL, comprising: MES, 50 mM (pH 5.5); EDTA, 2.5 mM; and DTT, 2.5 mM). Human cathepsin K (0.0906 pMoles in 25 µL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-Phe-Arg-AMC (4 nMoles in 25 µL of assay buffer) was added to the assay solutions and hydrolysis was followed spectrophotometrically at (λ 460 nm) for 5 minutes. Apparent inhibition constants ($K_i$) were calculated from the enzyme progress curves using standard mathematical models.

## EXAMPLE 14

## Cathepsin L Assay

Solutions of test compounds in varying concentrations were prepared in 10 µL of dimethyl sulfoxide (DMSO) and then diluted into assay buffer (40 µL, comprising: MES, 50 mM (pH 5.5); EDTA, 2.5 mM; and DTT, 2.5 mM). Human cathepsin L (0.05 pMoles in 25 µL of assay buffer) was added to the dilutions. The assay solutions were mixed for 5-10 seconds on a shaker plate, covered and incubated for 30 minutes at ambient temperature. Z-Phe-Arg-AMC (1 nMoles in 25 µL of assay buffer) was added to the assay

solutions and hydrolysis was followed spectrophotometrically at ($\lambda$ 460 nm) for 5 minutes. Apparent inhibition constants ($K_i$) were calculated from the enzyme progress curves using standard mathematical models.

Compounds of the invention were tested according to the above-described assays for protease inhibition and observed to exhibit selective cathepsin S inhibitory activity. For example, the compounds of the invention were found to inhibit cathepsin S protease activity at concentrations that are least 50 fold less than those concentrations required to produce an equiactive inhibition of cathepsin K protease activity. The apparent inhibition constants ($K_i$) for compounds of the invention range from about $10^{-10}$ to about $10^{-4}$ M.

## EXAMPLE 15

Representative Pharmaceutical Formulations Containing a Compound of Formula I

### ORAL FORMULATION

| | |
|---|---|
| Compound of Formula I | 10-100 mg |
| Citric Acid Monohydrate | 105 mg |
| Sodium Hydroxide | 18 mg |
| Flavoring | |
| Water | q.s. to 100 mL |

### INTRAVENOUS FORMULATION

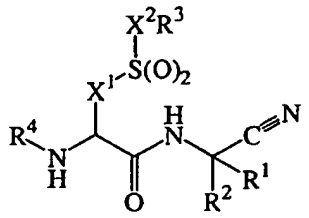
| | |
|---|---|
| Compound of Formula I | 0.1-10 mg |
| Dextrose Monohydrate | q.s. to make isotonic |
| Citric Acid Monohydrate | 1.05 mg |
| Sodium Hydroxide | 0.18 mg |
| Water for Injection | q.s. to 1.0 mL |

TABLET FORMULATION

| | |
|---|---|
| Compound of Formula I | 1% |
| Microcrystalline Cellulose | 73% |
| Stearic Acid | 25% |
| Colloidal Silica | 1%. |

WE CLAIM:

1. A compound of Formula I:



I

in which:

$X^1$ and $X^2$ are both methylene or $X^1$ is ethylene and $X^2$ is a bond;

$R^1$ is hydrogen and $R^2$ is cyano, hetero($C_5$)aryl or ($C_{1-4}$)alkyl-substituted hetero($C_5$)aryl or both $R^1$ and $R^2$ are hydrogen, halo, ($C_{1-4}$)alkyl or $-X^3OR^9$, wherein $X^3$ and $R^9$ are as defined below, or $R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-8}$)cycloalkylene or ($C_{3-8}$)heterocycloalkylene;

$R^3$ is $-CR^5=CHR^6$ or $-CR^7=NR^8$, wherein $R^5$ and $R^6$ together with the atoms to which $R^5$ and $R^6$ are attached form ($C_{2-6}$)alkenyl, ($C_{5-12}$)cycloalkenyl, hetero($C_{5-12}$)cycloalkenyl, ($C_{6-12}$)aryl, hetero($C_{6-12}$)aryl, ($C_{9-12}$)bicycloaryl or hetero($C_{8-12}$)bicycloaryl and $R^7$ and $R^8$ together with the atoms to which $R^7$ and $R^8$ are attached form hetero($C_{5-12}$)cycloalkenyl, hetero($C_{6-12}$)aryl or hetero($C_{8-12}$)bicycloaryl, wherein $R^3$ optionally is substituted by 1 to 5 radicals independently selected from a group consisting of ($C_{1-4}$)alkyl, cyano, halo, halo-substituted ($C_{1-4}$)alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or ($C_{1-2}$)alkylene, $R^9$ at each occurrence independently is hydrogen, ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{10}$ is ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and

$R^4$ is $-C(O)X^4R^{11}$ or $-S(O)_2X^4R^{11}$, wherein $X^4$ is a bond, -O- or $-NR^{12}-$, wherein $R^{12}$ is hydrogen or ($C_{1-6}$)alkyl, and $R^{11}$ is (i) ($C_{1-6}$)alkyl optionally substituted by $-OR^{13}$, $-SR^{13}$, $-S(O)R^{13}$, $-S(O)_2R^{13}$, $-C(O)R^{13}$, $-C(O)OR^{13}$, $-C(O)NR^{13}R^{14}$, $-NR^{13}R^{14}$, $-NR^{14}C(O)R^{13}$, $-NR^{14}C(O)OR^{13}$, $-NR^{14}C(O)NR^{13}R^{14}$ or $-NR^{14}C(NR^{14})NR^{13}R^{14}$, wherein $R^{13}$ is ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl,

hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl, ($C_{9-12}$)bicycloaryl($C_{0-3}$)alkyl or hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl and $R^{14}$ at each occurrence independently is hydrogen or ($C_{1-6}$)alkyl, or (ii) ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl, ($C_{9-12}$)bicycloaryl($C_{0-3}$)alkyl or hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl or (iii) ($C_{3-6}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-6}$)cycloalkyl($C_{0-3}$)alkyl, phenyl($C_{0-3}$)alkyl or hetero($C_{5-6}$)aryl($C_{0-3}$)alkyl substituted by $-X^5OR^{15}$, $-X^5SR^{15}$, $-X^5S(O)R^{15}$, $-X^5S(O)_2R^{15}$, $-X^5C(O)R^{15}$, $-X^5C(O)OR^{15}$, $-X^5C(O)NR^{15}R^{16}$, $-X^5NR^{15}R^{16}$, $-X^5NR^{16}C(O)R^{15}$, $-X^5NR^{16}C(O)OR^{15}$, $-X^5NR^{16}C(O)NR^{15}R^{16}$ or $-X^5NR^{16}C(NR^{16})NR^{15}R^{16}$, wherein $X^5$ is a bond or methylene, $R^{15}$ is ($C_{3-6}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-6}$)cycloalkyl($C_{0-3}$)alkyl, phenyl($C_{0-3}$)alkyl or hetero($C_{5-6}$)aryl($C_{0-3}$)alkyl and $R^{16}$ is hydrogen or ($C_{1-6}$)alkyl; wherein $R^4$ optionally further contains 1 to 5 substituents which when occurring within an alicyclic or aromatic ring system are radicals independently selected from a group consisting of ($C_{1-6}$)alkyl, ($C_{1-6}$)alkylidene, cyano, halo, nitro, halo-substituted ($C_{1-3}$)alkyl, $-X^5NR^{17}R^{17}$, $-X^5NR^{17}C(O)OR^{17}$, $-X^5NR^{17}C(O)NR^{17}R^{17}$, $-X^5NR^{17}C(NR^{17})NR^{17}R^{17}$, $-X^5OR^{17}$, $-X^5SR^{17}$, $-X^5C(O)OR^{17}$, $-X^5C(O)NR^{17}R^{17}$, $-X^5S(O)_2NR^{17}R^{17}$, $-X^5P(O)(OR^8)OR^{17}$, $-X^5OP(O)(OR^8)OR^{17}$, $-X^5NR^{17}C(O)R^{18}$, $-X^5S(O)R^{18}$, $-X^5S(O)_2R^{18}$ and $-X^5C(O)R^{18}$ and when occurring within an aliphatic moiety are radicals independently selected from a group consisting of cyano, halo, nitro, $-NR^{17}R^{17}$, $-NR^{17}C(O)OR^{17}$, $-NR^{17}C(O)NR^{17}R^{17}$, $-NR^{17}C(NR^{17})NR^{17}R^{17}$, $-OR^{17}$, $-SR^{17}$, $-C(O)OR^{17}$, $-C(O)NR^{17}R^{17}$, $-S(O)_2NR^{17}R^{17}$, $-P(O)(OR^{17})OR^{17}$, $-OP(O)(OR^{17})OR^{17}$, $-NR^{17}C(O)R^{18}$, $-S(O)R^{18}$, $-S(O)_2R^{18}$ and $-C(O)R^{18}$, wherein $X^5$ is a bond or ($C_{1-6}$)alkylene, $R^{17}$ at each occurrence independently is hydrogen, ($C_{1-6}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{18}$ is ($C_{1-6}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

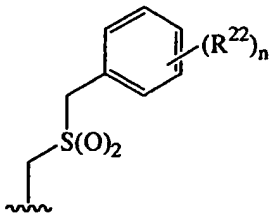
2. The compound of Claim 1 in which $R^1$ represents hydrogen and $R^2$ represents hydrogen, hetero($C_5$)aryl or ($C_{1-4}$)alkyl-substituted hetero($C_5$)aryl or $R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-5}$)cycloalkylene or ($C_{5-6}$)heterocycloalkylene; $X^1$ and $X^2$ are both methylene and $R^3$ represents ($C_{2-6}$)alkenyl, ($C_{6-12}$)aryl or hetero($C_{5-12}$)aryl, each optionally substituted by 1 to 5 radicals selected from a group consisting of ($C_{1-4}$)alkyl, cyano, halo, halo-substituted ($C_{1-4}$)alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or ($C_{1-2}$)alkylene, $R^9$ at each occurrence independently is hydrogen, ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{10}$ is ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and $R^4$ is $-C(O)X^4R^{11}$, wherein $X^4$ is a bond, -O- or -NH- and $R^{11}$ is ($C_{1-6}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-10}$)aryl($C_{0-3}$)alkyl or hetero($C_{5-10}$)aryl($C_{0-3}$)alkyl, wherein any heterocycloalkyl, aryl or heteroaryl group comprising $R^4$ optionally is substituted in the ring by $-X^5OR^{17}$, $-X^5NR^{17}C(O)OR^{17}$, $-X^5C(O)OR^{17}$ or $-X^5C(O)R^{18}$; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

3. The compound of Claim 2 in which $R^3$ more preferably represents biphenyl, isooxazolyl, naphthyl, phenyl, pyridyl, thienyl or vinyl, each optionally substituted by 1 to 5 radicals selected from a group consisting of ($C_{1-4}$)alkyl, cyano, halo, halo-substituted ($C_{1-4}$)alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or ($C_{1-2}$)alkylene, $R^9$ at each occurrence independently is hydrogen, ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{10}$ is ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

4. The compound of Claim 3 in which $R^3$ is biphenyl-2-yl, 2,4-bistrifluoromethylphenyl, 2,5-bistrifluoromethylphenyl, 4-*tert*-butylphenyl, 2-bromophenyl, 3-bromophenyl, 4-bromophenyl, 2-bromo-5-fluorophenyl, 3-chloro-2-fluorophenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 5-chlorothien-2-yl, 2-chloro-5-trifluoromethyl, 2-cyanophenyl, 3-cyanophenyl, 4-cyanophenyl, 1,5-dichlorophenyl, 2,6-dichlorophenyl, 3,4-dichlorophenyl, 2,3-difluorophenyl, 2,4-difluorophenyl, 3,4-difluorophenyl, 2-difluoromethoxyphenyl, 3-difluoromethoxyphenyl, 4-difluoromethoxyphenyl, 2,5-difluorophenyl, 2,6-difluorophenyl, 3,5-dimethylisooxaxol-4-yl, 3,5-dimethylphenyl, 2-fluoro-6-nitrophenyl, 2-fluorophenyl, 4-fluorophenyl, 2-fluoro-3-trifluoromethylphenyl, 2-fluoro-4-trifluoromethylphenyl, 2-fluoro-5-trifluoromethylphenyl, 2-fluoro-6-trifluoromethylphenyl, 4-fluoro-2-trifluoromethylphenyl, 4-fluoro-3-trifluoromethylphenyl, 2-iodophenyl, 3-iodophenyl, 4-iodophenyl, 2-methoxyphenyl, 4-methoxyphenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 3-methyl-2-fluorophenyl, naphth-2-yl, 2-nitrophenyl, 3-nitrophenyl, 4-nitrophenyl, 2,3,4,5,6-pentafluorophenyl, phenyl, prop-2-en-1-yl, pyrid-2-yl, pyrid-3-yl, pyrid-4-yl, 2-trifluoromethoxyphenyl, 3-trifluoromethoxyphenyl, 4-trifluoromethoxyphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, 2-trifluoromethylsulfanylphenyl, 3-trifluoromethylsulfanylphenyl, 4-trifluoromethylsulfanyl-phenyl, 2,3,4-trifluorophenyl, 2,3,5-trifluorophenyl, 2,4,6-trifluorophenyl, 2,4,5-trifluorophenyl or 2,3,6-trifluorophenyl; and $R^4$ is 3-acetylbenzoyl, allyloxycarbonyl, 2-aminopyrid-3-ylcarbonyl, 6-aminopyrid-3-ylcarbonyl, benzo[1,3]dioxol-5-ylcarbonyl, benzoyl, 4-benzoylbenzoylcarbonyl, benzo[1,3]dioxol-3-ylcarbonyl, benzofur-2-ylcarbonyl, biphenyl-4-ylcarbonyl, 4-bromobenzoyl, 3-bromothien-2-yl, *tert*-butoxycarbonyl, 3-*tert*-butoxycarbonylaminomethylbenzoyl, 4-*tert*-butoxycarbonylpiperazin-1-ylcarbonyl, 3-chlorobenzoyl, 4-chlorobenzoyl, 3-chlorothienylcarbonyl, cyclopentylcarbonyl, 3,4-difluorobenzoyl, 3,4-dimethoxybenzoyl, dimethylcarbamoyl, 4-ethoxycarbonylpiperazin-1-ylcarbonyl, 4-fluorobenzoyl, 3-fluoro-4-methoxybenzoyl, fur-2-ylcarbonyl, fur-3-ylcarbonyl, 4-fur-2-ylcarbonylpiperazin-1-ylcarbonyl, 3-hydroxybenzoyl, 4-hydroxybenzoyl, 4-hydroxypyrid-3-yl, 6-hydroxypyrid-3-yl, 1*H*-indol-4-ylcarbonyl, isopropylcarbamoyl,

isobutyloxycarbonyl, isopropyloxycarbonyl, 3-methoxybenzoyl, 4-methoxybenzoyl, 3-methylbenzoyl, 5-methylthienylcarbonyl, 4-methylvaleryl, morpholin-4-ylcarbonyl, naphth-2-ylcarbonyl, naphth-2-ylsulfonyl, 3-phenoxybenzoyl, 3-phenylacryloyl, phenylsulfonyl, pyrazin-2-ylcarbonyl, 3-pyrid-3-ylacryl, pyrid-2-ylcarbonyl, pyrid-3-ylcarbonyl, pyrid-4-ylcarbonyl, quinol-2-ylcarbonyl, quinol-3-ylcarbonyl, thien-2-ylcarbonyl, thien-3-ylcarbonyl, thien-2-ylsulfonyl, 4-trifluoromethoxybenzoyl or 4-trifluoromethylbenzoyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

5. The compound of Claim 3 in which $X^1$, $X^2$ and $R^3$ along with the sulfonyl moiety to which $X^1$ and $X^2$ are attached together represent a group having the following formula:




in which n is 0, 1, 2, 4 or 5 and $R^{22}$ at each occurrence independently is selected from a group consisting of $(C_{1-4})$alkyl, cyano, halo, halo-substituted $(C_{1-4})$alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or $(C_{1-2})$alkylene, $R^9$ at each occurrence independently is hydrogen, $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl and $R^{10}$ is $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl; and $R^4$ is benzoyl, morpholin-4-ylcarbonyl, thien-2-yl, thien-3-yl, indol-4-yl and pyridin-4-yl, respectively, optionally substituted in the ring by 1 to 2 substituents selected from fluoro and methyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such

compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

6. The compound of Claim 5 in which n is 0, 1 or 2 and $R^{22}$ at each occurrence independently is selected from a group consisting of $(C_{1-4})$alkyl, cyano, halo, halo-substituted $(C_{1-4})$alkyl, nitro, $-OR^9$, $-SR^9$ and $-C(O)OR^9$, wherein $R^9$ at each occurrence independently is hydrogen, $(C_{1-3})$alkyl or halo-substituted $(C_{1-3})$alkyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

7. The compound of Claim 6 in which $R^{22}$ at each occurrence independently is selected from a group consisting of $(C_{1-4})$alkyl, bromo, carboxy, chloro, cyano, difluoromethoxy, fluoro, iodo, methoxy, nitro, trifluoromethoxy, trifluoromethyl and trifluorosulfanyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

8. The compound of Claim 7 in which $R^{22}$ at the first occurrence is attached at the ring carbon ortho or meta to the 1-position of the phenyl moiety; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

9. The compound of Claim 8 selected from a group consisting of:

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-isonicotinamide;

Pyridine-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

Pyrazine-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-6-hydroxy-nicotinamide;

2-Amino-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide;

6-Amino-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-nicotinamide;

3-Hydroxy-pyridine-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

Morpholine-4-carboxylic acid-{(R)-1-(4-cyano-tetrahydro-pyran-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

Morpholine-4-carboxylic acid-{(R)-1-(4-cyano-1-methyl-piperidin-4-ylcarbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

(R)-*N* -Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(3, 3-dimethyl-ureido)-propionamide;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid allyl ester;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid isopropyl ester;

{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-carbamic acid isobutyl ester;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3,4-difluoro-benzamide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethane-sulfonyl]-ethyl}-3-methyl-benzamide;

Thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-

difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

4-Bromo-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-benzamide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-4-methoxy-benzamide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-4-trifluoromethoxy-benzamide;

Naphthalene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

(E)-*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-phenyl-acrylamide;

5-Methyl-thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

Biphenyl-4-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

1H-Indole-5-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

Benzo[1,3]dioxole-5-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

Benzo[b]thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-phenoxy-benzamide;

Quinoline-3-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-(1-phenyl-methanoyl)-benzamide;

4-Chloro-N-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-benzamide;

*N*-{(R)-1-(Cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-3-fluoro-4-methoxy-benzamide;

3-Bromo-thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

3-Chloro-benzo[b]thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

3-Chloro-thiophene-2-carboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

*N*-{(R)-(Cyanomethyl-carbamoyl)-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-trifluoromethyl-benzamide;

(R)-*N*-Cyanomethyl-3-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-2-(naphthalene-2-sulfonylamino)-propionamide;

Cyclopentanecarboxylic acid-{(R)-1-(cyanomethyl-carbamoyl)-2-[2-(1,1-difluoro-methoxy)-phenylmethanesulfonyl]-ethyl}-amide;

*N*-[1R-cyanomethylcarbamoyl-2-(3-trifluoromethoxybenzylsulfonyl)ethyl]benzamide;

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]benzamide;

*N*-[1R-cyanomethylcarbamoyl-2-(2-trifluoromethoxybenzylsulfonyl)ethyl]benzamide;

*N*-(1R-cyanomethylcarbamoyl-2-(3-difluoromethoxybenzylsulfonyl)ethyl]benzamide;

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)ethyl]morpholine-4-carboxamide;

*N*-[1R-(1-cyanocyclopropylcarbamoyl)-2-(2-difluoromethoxybenzylsulfonyl)ethyl]-morpholine-4-carboxamide; and

*N*-[1*R*-cyanomethylcarbamoyl)-2-(3-iodobenzylsulfonyl)ethyl]benzamide; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

10. The compound of Claim 9 selected from a group consisting of:

*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)-ethyl]benzamide;

*N*-[1R-cyanomethylcarbamoyl-2-(2-trifluoromethoxybenzylsulfonyl)-ethyl]benzamide;

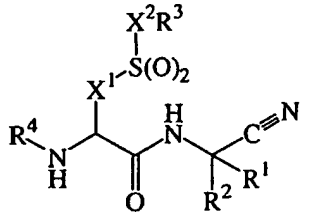
*N*-[1R-cyanomethylcarbamoyl-2-(2-difluoromethoxybenzylsulfonyl)-ethyl]morpholine-4-carboxamide;

*N*-[1R-(1-cyanocyclopropylcarbamoyl)-2-(2-difluoromethoxybenzylsulfonyl)-ethyl]morpholine-4-carboxamide; and the N-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

11. A pharmaceutical composition comprising a therapeutically effective amount of a compound of Claim 1 in combination with a pharmaceutically acceptable excipient.

12. A method for treating a disease in an animal in which inhibition cathepsin S can prevent, inhibit or ameliorate the pathology and/or symptomatology of the disease, which method comprises administering to the animal a therapeutically effective amount of compound of Claim 1 or a *N*-oxide derivative or individual isomer or mixture of isomers thereof; or a pharmaceutically acceptable salt or solvate of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof.

13 The use of a compound of Formula I:



I

in which:

$X^1$ and $X^2$ are both methylene or $X^1$ is ethylene and $X^2$ is a bond;

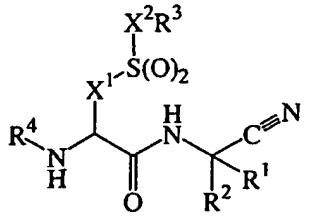
$R^1$ is hydrogen and $R^2$ is cyano, hetero($C_5$)aryl or ($C_{1-4}$)alkyl-substituted hetero($C_5$)aryl or both $R^1$ and $R^2$ are hydrogen, halo, ($C_{1-4}$)alkyl or $-X^3OR^9$, wherein $X^3$ and $R^9$ are as defined below, or $R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-8}$)cycloalkylene or ($C_{3-8}$)heterocycloalkylene;

$R^3$ is $-CR^5=CHR^6$ or $-CR^7=NR^8$, wherein $R^5$ and $R^6$ together with the atoms to which $R^5$ and $R^6$ are attached form ($C_{2-6}$)alkenyl, ($C_{5-12}$)cycloalkenyl, hetero($C_{5-12}$)cycloalkenyl, ($C_{6-12}$)aryl, hetero($C_{6-12}$)aryl, ($C_{9-12}$)bicycloaryl or hetero($C_{8-12}$)bicycloaryl and $R^7$ and $R^8$ together with the atoms to which $R^7$ and $R^8$ are attached form hetero($C_{5-12}$)cycloalkenyl, hetero($C_{6-12}$)aryl or hetero($C_{8-12}$)bicycloaryl, wherein $R^3$ optionally is substituted by 1 to 5 radicals independently selected from a group consisting of ($C_{1-4}$)alkyl, cyano, halo, halo-substituted ($C_{1-4}$)alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or ($C_{1-2}$)alkylene, $R^9$ at each occurrence independently is hydrogen, ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{10}$ is ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and

$R^4$ is $-C(O)X^4R^{11}$ or $-S(O)_2X^4R^{11}$, wherein $X^4$ is a bond, -O- or $-NR^{12}-$, wherein $R^{12}$ is hydrogen or ($C_{1-6}$)alkyl, and $R^{11}$ is (i) ($C_{1-6}$)alkyl optionally substituted by $-OR^{13}$, $-SR^{13}$, $-S(O)R^{13}$, $-S(O)_2R^{13}$, $-C(O)R^{13}$, $-C(O)OR^{13}$, $-C(O)NR^{13}R^{14}$, $-NR^{13}R^{14}$, $-NR^{14}C(O)R^{13}$, $-NR^{14}C(O)OR^{13}$, $-NR^{14}C(O)NR^{13}R^{14}$ or $-NR^{14}C(NR^{14})NR^{13}R^{14}$, wherein $R^{13}$ is ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl, ($C_{9-12}$)bicycloaryl($C_{0-3}$)alkyl or hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl and $R^{14}$ at each occurrence independently is hydrogen or ($C_{1-6}$)alkyl, or (ii) ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl,

$(C_{9-12})$bicycloaryl$(C_{0-3})$alkyl or hetero$(C_{8-12})$bicycloaryl$(C_{0-3})$alkyl or (iii) $(C_{3-6})$cycloalkyl$(C_{0-3})$alkyl, hetero$(C_{5-6})$cycloalkyl$(C_{0-3})$alkyl, phenyl$(C_{0-3})$alkyl or hetero$(C_{5-6})$aryl$(C_{0-3})$alkyl substituted by $-X^5OR^{15}$, $-X^5SR^{15}$, $-X^5S(O)R^{15}$, $-X^5S(O)_2R^{15}$, $-X^5C(O)R^{15}$, $-X^5C(O)OR^{15}$, $-X^5C(O)NR^{15}R^{16}$, $-X^5NR^{15}R^{16}$, $-X^5NR^{16}C(O)R^{15}$, $-X^5NR^{16}C(O)OR^{15}$, $-X^5NR^{16}C(O)NR^{15}R^{16}$ or $-X^5NR^{16}C(NR^{16})NR^{15}R^{16}$, wherein $X^5$ is a bond or methylene, $R^{15}$ is $(C_{3-6})$cycloalkyl$(C_{0-3})$alkyl, hetero$(C_{5-6})$cycloalkyl$(C_{0-3})$alkyl, phenyl$(C_{0-3})$alkyl or hetero$(C_{5-6})$aryl$(C_{0-3})$alkyl and $R^{16}$ is hydrogen or $(C_{1-6})$alkyl; wherein $R^4$ optionally further contains 1 to 5 substituents which when occurring within an alicyclic or aromatic ring system are radicals independently selected from a group consisting of $(C_{1-6})$alkyl, $(C_{1-6})$alkylidene, cyano, halo, nitro, halo-substituted $(C_{1-3})$alkyl, $-X^5NR^{17}R^{17}$, $-X^5NR^{17}C(O)OR^{17}$, $-X^5NR^{17}C(O)NR^{17}R^{17}$, $-X^5NR^{17}C(NR^{17})NR^{17}R^{17}$, $-X^5OR^{17}$, $-X^5SR^{17}$, $-X^5C(O)OR^{17}$, $-X^5C(O)NR^{17}R^{17}$, $-X^5S(O)_2NR^{17}R^{17}$, $-X^5P(O)(OR^8)OR^{17}$, $-X^5OP(O)(OR^8)OR^{17}$, $-X^5NR^{17}C(O)R^{18}$, $-X^5S(O)R^{18}$, $-X^5S(O)_2R^{18}$ and $-X^5C(O)R^{18}$ and when occurring within an aliphatic moiety are radicals independently selected from a group consisting of cyano, halo, nitro, $-NR^{17}R^{17}$, $-NR^{17}C(O)OR^{17}$, $-NR^{17}C(O)NR^{17}R^{17}$, $-NR^{17}C(NR^{17})NR^{17}R^{17}$, $-OR^{17}$, $-SR^{17}$, $-C(O)OR^{17}$, $-C(O)NR^{17}R^{17}$, $-S(O)_2NR^{17}R^{17}$, $-P(O)(OR^{17})OR^{17}$, $-OP(O)(OR^{17})OR^{17}$, $-NR^{17}C(O)R^{18}$, $-S(O)R^{18}$, $-S(O)_2R^{18}$ and $-C(O)R^{18}$, wherein $X^5$ is a bond or $(C_{1-6})$alkylene, $R^{17}$ at each occurrence independently is hydrogen, $(C_{1-6})$alkyl or halo-substituted $(C_{1-3})$alkyl and $R^{18}$ is $(C_{1-6})$alkyl or halo-substituted $(C_{1-3})$alkyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; in the manufacture of a medicament for treating a disease in an animal in which cathepsin S activity contributes to the pathology and/or symptomatology of the disease.

14. A process for preparing a compound of Formula I:



I

in which:

$X^1$ and $X^2$ are both methylene or $X^1$ is ethylene and $X^2$ is a bond;

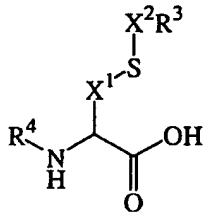
$R^1$ is hydrogen and $R^2$ is cyano, hetero($C_5$)aryl or ($C_{1-4}$)alkyl-substituted hetero($C_5$)aryl or both $R^1$ and $R^2$ are hydrogen, halo, ($C_{1-4}$)alkyl or $-X^3OR^9$, wherein $X^3$ and $R^9$ are as defined below, or $R^1$ and $R^2$ together with the carbon atom to which both $R^1$ and $R^2$ are attached form ($C_{3-8}$)cycloalkylene or ($C_{3-8}$)heterocycloalkylene;

$R^3$ is $-CR^5=CHR^6$ or $-CR^7=NR^8$, wherein $R^5$ and $R^6$ together with the atoms to which $R^5$ and $R^6$ are attached form ($C_{2-6}$)alkenyl, ($C_{5-12}$)cycloalkenyl, hetero($C_{5-12}$)cycloalkenyl, ($C_{6-12}$)aryl, hetero($C_{6-12}$)aryl, ($C_{9-12}$)bicycloaryl or hetero($C_{8-12}$)bicycloaryl and $R^7$ and $R^8$ together with the atoms to which $R^7$ and $R^8$ are attached form hetero($C_{5-12}$)cycloalkenyl, hetero($C_{6-12}$)aryl or hetero($C_{8-12}$)bicycloaryl, wherein $R^3$ optionally is substituted by 1 to 5 radicals independently selected from a group consisting of ($C_{1-4}$)alkyl, cyano, halo, halo-substituted ($C_{1-4}$)alkyl, nitro, $-X^3NR^9R^9$, $-X^3OR^9$, $-X^3SR^9$, $-X^3C(O)NR^9R^9$, $-X^3C(O)OR^9$, $-X^3S(O)R^{10}$, $-X^3S(O)_2R^{10}$ and $-X^3C(O)R^{10}$, wherein $X^3$ is a bond or ($C_{1-2}$)alkylene, $R^9$ at each occurrence independently is hydrogen, ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl and $R^{10}$ is ($C_{1-3}$)alkyl or halo-substituted ($C_{1-3}$)alkyl; and

$R^4$ is $-C(O)X^4R^{11}$ or $-S(O)_2X^4R^{11}$, wherein $X^4$ is a bond, -O- or $-NR^{12}-$, wherein $R^{12}$ is hydrogen or ($C_{1-6}$)alkyl, and $R^{11}$ is (i) ($C_{1-6}$)alkyl optionally substituted by $-OR^{13}$, $-SR^{13}$, $-S(O)R^{13}$, $-S(O)_2R^{13}$, $-C(O)R^{13}$, $-C(O)OR^{13}$, $-C(O)NR^{13}R^{14}$, $-NR^{13}R^{14}$, $-NR^{14}C(O)R^{13}$, $-NR^{14}C(O)OR^{13}$, $-NR^{14}C(O)NR^{13}R^{14}$ or $-NR^{14}C(NR^{14})NR^{13}R^{14}$, wherein $R^{13}$ is ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl, ($C_{9-12}$)bicycloaryl($C_{0-3}$)alkyl or hetero($C_{8-12}$)bicycloaryl($C_{0-3}$)alkyl and $R^{14}$ at each occurrence independently is hydrogen or ($C_{1-6}$)alkyl, or (ii) ($C_{3-12}$)cycloalkyl($C_{0-3}$)alkyl, hetero($C_{5-12}$)cycloalkyl($C_{0-3}$)alkyl, ($C_{6-12}$)aryl($C_{0-3}$)alkyl, hetero($C_{5-12}$)aryl($C_{0-3}$)alkyl,

$(C_{9-12})$bicycloaryl$(C_{0-3})$alkyl or hetero$(C_{8-12})$bicycloaryl$(C_{0-3})$alkyl or (iii) $(C_{3-6})$cycloalkyl$(C_{0-3})$alkyl, hetero$(C_{5-6})$cycloalkyl$(C_{0-3})$alkyl, phenyl$(C_{0-3})$alkyl or hetero$(C_{5-6})$aryl$(C_{0-3})$alkyl substituted by $-X^5OR^{15}$, $-X^5SR^{15}$, $-X^5S(O)R^{15}$, $-X^5S(O)_2R^{15}$, $-X^5C(O)R^{15}$, $-X^5C(O)OR^{15}$, $-X^5C(O)NR^{15}R^{16}$, $-X^5NR^{15}R^{16}$, $-X^5NR^{16}C(O)R^{15}$, $-X^5NR^{16}C(O)OR^{15}$, $-X^5NR^{16}C(O)NR^{15}R^{16}$ or $-X^5NR^{16}C(NR^{16})NR^{15}R^{16}$, wherein $X^5$ is a bond or methylene, $R^{15}$ is $(C_{3-6})$cycloalkyl$(C_{0-3})$alkyl, hetero$(C_{5-6})$cycloalkyl$(C_{0-3})$alkyl, phenyl$(C_{0-3})$alkyl or hetero$(C_{5-6})$aryl$(C_{0-3})$alkyl and $R^{16}$ is hydrogen or $(C_{1-6})$alkyl; wherein $R^4$ optionally further contains 1 to 5 substituents which when occurring within an alicyclic or aromatic ring system are radicals independently selected from a group consisting of $(C_{1-6})$alkyl, $(C_{1-6})$alkylidene, cyano, halo, nitro, halo-substituted $(C_{1-3})$alkyl, $-X^5NR^{17}R^{17}$, $-X^5NR^{17}C(O)OR^{17}$, $-X^5NR^{17}C(O)NR^{17}R^{17}$, $-X^5NR^{17}C(NR^{17})NR^{17}R^{17}$, $-X^5OR^{17}$, $-X^5SR^{17}$, $-X^5C(O)OR^{17}$, $-X^5C(O)NR^{17}R^{17}$, $-X^5S(O)_2NR^{17}R^{17}$, $-X^5P(O)(OR^8)OR^{17}$, $-X^5OP(O)(OR^8)OR^{17}$, $-X^5NR^{17}C(O)R^{18}$, $-X^5S(O)R^{18}$, $-X^5S(O)_2R^{18}$ and $-X^5C(O)R^{18}$ and when occurring within an aliphatic moiety are radicals independently selected from a group consisting of cyano, halo, nitro, $-NR^{17}R^{17}$, $-NR^{17}C(O)OR^{17}$, $-NR^{17}C(O)NR^{17}R^{17}$, $-NR^{17}C(NR^{17})NR^{17}R^{17}$, $-OR^{17}$, $-SR^{17}$, $-C(O)OR^{17}$, $-C(O)NR^{17}R^{17}$, $-S(O)_2NR^{17}R^{17}$, $-P(O)(OR^{17})OR^{17}$, $-OP(O)(OR^{17})OR^{17}$, $-NR^{17}C(O)R^{18}$, $-S(O)R^{18}$, $-S(O)_2R^{18}$ and $-C(O)R^{18}$, wherein $X^5$ is a bond or $(C_{1-6})$alkylene, $R^{17}$ at each occurrence independently is hydrogen, $(C_{1-6})$alkyl or halo-substituted $(C_{1-3})$alkyl and $R^{18}$ is $(C_{1-6})$alkyl or halo-substituted $(C_{1-3})$alkyl; and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; and pharmaceutically acceptable salts and solvates of such compounds and the *N*-oxide derivatives, prodrug derivatives, protected derivatives, individual isomers and mixtures of isomers thereof; which processes comprises:

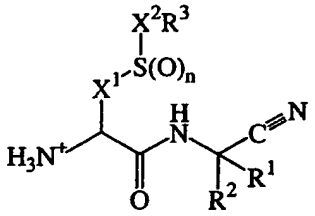
(A) reacting a compound of Formula 2:



2

with a compound of the formula $NH_2CR^1R^2CN$, in which $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in the Summary of the Invention for Formula I; or

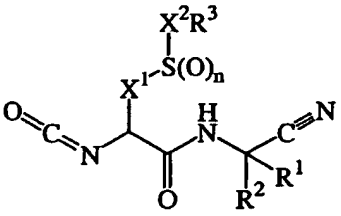
(B) reacting a compound of Formula 3:



3

with a compound of the formula $R^4L$, in which n is 0 or 2, L is a leaving group and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in the Summary of the Invention for Formula I, and then oxidizing when n is 0; or

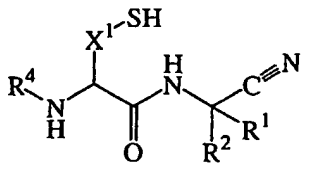
(C) reacting a compound of Formula 4:



4

with a compound of formula $NHR^{13}R^{14}$ or $NHR^{20}R^{21}$ to provide a compound of Formula I in which $R^4$ is $-C(O)NR^{13}R^{14}$ or $-C(O)NR^{20}R^{21}$, respectively, wherein n is 0 or 2, $R^{20}$ and $R^{21}$ together with the nitrogen atom to which $R^{20}$ and $R^{21}$ are attached form hetero($C_{5-12}$)cycloalkyl and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$, $R^{13}$ and $R^{14}$ are as defined in the Summary of the Invention for Formula I, and then oxidizing when n is 0; or

(D) reacting a compound of Formula 5:



5

with a compound of $R^3X^2L$ in which L is a leaving group and each $X^1$, $X^2$, $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in the Summary of the Invention for Formula I; and

(E) optionally converting a compound of Formula I into a pharmaceutically acceptable salt;

(F) optionally converting a salt form of a compound of Formula I to non-salt form;

(G) optionally converting an unoxidized form of a compound of Formula I into a pharmaceutically acceptable *N*-oxide;

(H) optionally converting an *N*-oxide form of a compound of Formula I its unoxidized form;

(I) optionally resolving an individual isomer of a compound of Formula I from a mixture of isomers;

(J) optionally converting a non-derivatized compound of Formula I into a pharmaceutically prodrug derivative; and

(K) optionally converting a prodrug derivative of a compound of Formula I to its non-derivatized form.

# INTERNATIONAL SEARCH REPORT

Interr nal Application No
PCT/US 00/25415

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D213/82 C07D213/81 C07D295/20 C07D333/40 C07D333/70
C07D209/08 C07D317/68 C07D215/54 C07D215/48 C07C317/28
A61K31/5375 A61K31/5377 A61K31/455 A61K31/47 A61K31/4965

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | PICKEN P P ET AL: "Inhibition of bovine cathepsin B by amino acid-derived nitriles" BIOCHEMICAL SOCIETY TRANSACTIONS,COLCHESTER, ESSEX,GB, vol. 18, no. 2, April 1990 (1990-04), page 316 XP002108054 ISSN: 0300-5127 left-hand column, paragraph "Experimental", compound "benzyloxycarbonyl-L-(S-Benzyl)-cysteinyl-aminoacetonitrile" table 1 --- -/-- | 1-3,5, 11-13 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 28 December 2000 | 05/01/2001 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Hass, C |

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Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Inter al Application No
PCT/US 00/25415

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K31/381 A61P19/02 A61P33/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | EP 0 652 009 A (LILLY CO ELI; ATHENA NEUROSCIENCES INC (US)) 10 May 1995 (1995-05-10) page 99, line 29 -page 100, line 4; claims 1-3; example 117 abstract | 1-3,5, 11-13 |
| A | WO 98 23588 A (BRITISH BIOTECH PHARM; FLOYD CHRISTOPHER DAVID (GB)) 4 June 1998 (1998-06-04) page 1, line 1 -page 2, line 3; claims 1,20; examples 3,6 | 1-3,5,11 |
| A | US 5 852 007 A (CHATTERJEE SANKAR) 22 December 1998 (1998-12-22) claims 1,32,38; example 66 | 1-3,5,11 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 28 December 2000 | |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Hass, C |

2

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A,P | WO 00 51998 A (BOEHRINGER INGELHEIM PHARMA) 8 September 2000 (2000-09-08) abstract; claims 21,31,45-49; examples 1,2 --- | 1,11-13 |
| A | S. CHATTERJEE ET AL.: "D-Amino Acid Containing, High-Affinity Inhibitors of Recombinant Human Calpain I" JOURNAL OF MEDICINAL CHEMISTRY, vol. 41, no. 15, 16 July 1998 (1998-07-16), pages 2663-6, XP002155160 table 2, compound 23 --- | 1 |
| A | JP 63 301868 A (NIPPON KAYAKU CO LTD) 8 December 1988 (1988-12-08) page 779(7), compound no. 51 ----- | 1 |

2

# INTERNATIONAL SEARCH REPORT

formation on patent family members

Inter ial Application No
PCT/US 00/25415

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0652009 A | 10-05-1995 | AU 6897094 A | 16-02-1995 |
| | | CA 2129689 A | 10-02-1995 |
| | | CN 1120040 A | 10-04-1996 |
| | | CZ 9401841 A | 15-03-1995 |
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